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NON-EQUILIBRIUM STATISTICAL MECHANICS OF SIMPLE DENSE FLUIDS

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INTRODUCTION

One of the most active fields of research in the past fifteen years has been the study of the molecular theory of irreversible processes. The basic problems to be solved can be phrased in terms of two questions: (a) How do the time reversible equations of motion lead to a description of the approach to equilibrium? (b) Given a technique for describing the approach to equilibrium, what is the relationship between the macroscopic transport coefficients and the properties of the molecules of which a system is composed.

In the forefront of the efforts to answer question (a) has been the work of Prigogine and co-workers.[1,2] They proceed by writing an infinite order perturbation solution to the Liouville equation. It is found that the ordinary phase space representation of the N-particle distribution function is much too cumbersome, and that a transformation to a new representation facilitates much of the ensuing analysis. By chosing as a basis set the eigenfunctions of the free particle Liouville operator, Prigogine and co-workers, solve the Liouville equation much as Dirac solves the time dependent Schroedinger equation.

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1. I. Prigogine, Non-equilibrium Statistical Mechanics (Interscience Publishers, Ltd., London, 1962).

2. R. Balescu, Statistical Mechanics of Charged Particles (Interscience Publishers, Ltd., London, 1963).

The eigenfunctions of the free particle Liouville operator are plane waves, and the solution of the full Liouville equation, in terms of this basis set, amounts to a Fourier expansion of the N-particle distribution function in a complete set of plane waves. Thus the representation chosen is ($\underline{k}$, $\underline{p}$) instead of ($\underline{r}$, $\underline{p}$). The main assumption of Prigogine and collaborators is the following: The N-particle distribution function which describes the initial state must have the property that all reduced distribution functions remain finite in the limit $N \longrightarrow \infty$, $V \longrightarrow \infty$, such that $\frac{N}{V}$ is finite and constant, where N is the number of particles and V the volume of the system. In this limit, the spectrum of $\underline{k}$ becomes continuous and sums over $\underline{k}$ may be replaced by integrals. A further assumption of Prigogine and co-workers is that the N-particle distribution function conforms to periodic boundary conditions. It is then possible to identify the Fourier coefficients of the expansion with the Fourier transforms of the Ursell functions in a cluster expansion of the N-particle distribution function. Thus, a connection is made between the lower order Fourier coefficients and the lower order reduced distribution functions. Prigogine and co-workers argue, as have Born, Green,[3] Yvon,[4] Kirkwood[5] and Bogolubov,[6] that since irreversibility appears in

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3. M. Born and H. S. Green, A General Kinetic Theory of Liquids (Cambridge University Press, London, 1949).

4. J. Yvon, Actualites Scientifique et Industrielles (Hermann et Cie, Paris, 1958).

5. J. G. Kirkwood, J. Chem. Phys. **14**, 180 (1946).

6. N. Bogolubov, J. Phys. (U.S.S.R.) **10**, 265 (1946).

the thermodynamic functions, and since these functions are determined by the reduced distribution functions, the reduced distributions must evolve irreversibly in time. They then derive equations for the evolution of the Fourier components, or what is tantamount to this, for the evolution of the reduced distribution functions. These equations are general. They are non-Markovian in structure and contain a term which describes the destruction of the correlations. The equations are reversible and are, therefore, consistent with the reversible equations of motion. At this point, Prigogine assumes that after a very short time the system forgets the initial correlations--correlations are destroyed. Thus, a set of non-Markovian evolution equations are derived. These equations have been used successfully to predict the non-Markovian effects in a ferromagnetic spin system. When it is assumed that the Fourier components do not change very much over the duration of a collision, Markovian or Boltzmann-like equations are obtained. It is found that Markovian equations are valid for the prediction of steady state phenomena, but are not valid for the description of time dependent processes such as occur in the presence of a time dependent external force, or the approach to equilibrium of the distribution function. Using an Enskog-Hilbert iterative procedure, Resibois and Prigogine[7] have shown that the Kubo relations[8] can be retrieved from the master equation in the linear-Markovian

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7. P. Resibois and I. Prigogine (private communication).

8. R. Kubo, Lectures Theor. Phys. (Boulder) I, 120-203.

approximation. The Prigogine theory constitutes the greatest single advance in the theory of irreversible processes in this century.

In principle, a solution of problem (a) also provides a solution to problem (b). For once given the non-equilibrium distribution function, the fluxes of matter momentum and energy are readily obtained. In practice, the Prigogine theory, as presently written, cannot be used for the treatment of dense fluids because it is basically a perturbation expansion carried to infinite order. The method is useful for weakly interacting systems where the ratio of the interaction energy to kT provides a small expansion parameter, or for very dilute systems, where the range of the potential divided by the mean free path provides a small expansion parameter. In a liquid, however, every molecule is in continuous interaction with all its neighbors, and neither of the parameters mentioned is useful. It is the absence of a small parameter which accounts for most of the difficulty in treating dense fludis. The main difficulty resides in the fact that Prigogine has used the free-particle Liouville operator as his unperturbed state. The free-particle operator is indeed a very poor approximation to the real dense fluid operator. Whereas it is a very good approximation for very dilute systems. Thus the perturbation series converges less rapidly the higher the density with this choice of the unperturbed operator. The obvious thing to do would be to select an unperturbed operator which is, in fact, closer to the true operator. This is not a trivial task. There are immense difficulties in solving the Liouville equation for anything other than for the case of noninteracting particles. A more realistic unperturbed operator might be the hard core operator, or the Maxwell Molecule operator. These are, of course, highly idealized choices, but they might work. Nothing like this has yet been done.

The only successful treatment of dissipation in the dense fluid phase is based upon ideas which were introduced by Kirkwood.[5] The guiding principle of Kirkwood's analysis is the description of the lower order reduced distribution functions only on a time scale such that a meaningful independent dynamical event can be defined. Transient effects during the establishment of the steady state and the approach to the steady state must be discussed using other techniques. Rapidly oscillating external fields cannot be understood by these methods. We must first note that a complete cluster expansion of the integro-differential equation describing the N-body distribution function can be obtained from a Kirkwood type analysis, i.e. by use of coarse graining in time. In the steady state the resultant equations are identical with those derived by Prigogine, by Bogolubov and by Green. This may be taken as confirmation of Kirkwood's intuitive approach to problems concerning the steady state. Kirkwood proposed to describe the motion of a molecule in a liquid as a quasi-Brownian motion. He then derived Fokker-Planck equations for the singlet and doublet distribution functions using the assumption that the mean momentum transfer due to the fluctuating intermolecular force field was small relative to the mean momentum, and that the force acting on a specific particle due to its neighbors has a correlation time which is much smaller than the correlation time of the momentum of that particle, i.e. the force on a particle fluctuates many times while the momentum of that particle remains fairly constant. This analysis has been criticized on the ground that large momentum transfers occur during strongly repulsive encounters. It is interesting that the Kirkwood relation between the friction coefficient and the autocorrelation function of the force acting on a molecule—probably the most valuable result of the analysis—when applied to the rigid sphere fluid gives the same result as the Enskog theory. Nevertheless, the existence of a very short range repulsive force contribution and a somewhat longer range attractive force contribution to the total intermolecular force suggests that a distinction can be made between large and small momentum transfers.

Rice and Allnatt[9,10] have constructed a theory of transport within the framework of the Kirkwood philosophy. The theory divides the dissipative forces into hard and soft contributions and uses suitable but different dynamical descriptions for the two contributions. It is assumed that:

a. The intermolecular pair potential may be represented by a rigid core with a superposed soft potential. The soft potential may have both repulsive and attractive

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9. S. A. Rice, A. Allnatt, J. Chem. Phys. 34, 2144 (1961).
10. A. Allnatt, S. A. Rice, J. Chem. Phys. 34, 2156 (1961).

parts provided only that the range is large relative to the range of a rigid core.

b. There exists a time τ such that

1. $\tau_f \ll \tau < \tau_p$ where τ_f and τ_p are the force and momentum correlation times

2. a dynamical event in τ is independent of a prior dynamical event τ earlier

c. The basic dynamical event in a liquid consists of a rigid core encounter followed by quasi-Brownian motion in the rapidly fluctuating force field of the surrounding molecules.

The analysis yields integro-differential equations for the singlet and doublet distribution functions; the hard core contribution leads to an Enskog—like modified Boltzmann collision kernel, while the fluctuating force component gives rise to a Fokker-Planck term characterized by a friction coefficient defined by the soft force only.

The consequences of the Rice-Allnatt theory for the special cases of the ion mobility, thermal conductivity and shear viscosity have been examined by Rice and colleagues.[11-15] For

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11. H. Davis, S. A. Rice, and L. Meyer, J. Chem. Phys. <u>37</u>, 947 (1962).

12. H. Davis, S. A. Rice, and L. Meyer, J. Chem. Phys. <u>37</u>, 2470 (1962).

13. H. Davis, S. A. Rice, and L. Meyer, J. Chem. Phys. <u>37</u>, 1521 (1962).

14. L. Ikenberry, S. A. Rice, J. Chem. Phys. <u>39</u>, 1561 (1963).

15. B. Lowry, S. A. Rice, and P. Gray, J. Chem. Phys. <u>40</u>, 3673 (1964).

simple dense fluids all the cases cited good agreement with experiment is obtained. At present, it appears that the Rice-Allnatt theory provides a fairly good qualitative and quantitative description of linear transport processes in simple liquids; but the truth of this statement can only be fully ascertained when adequate equilibrium data become available. The agreement between theory and experiment cannot at present be fully judged because of the lack of accurate equilibrium pair correlation functions.

There have been other attempts to describe the transport processes in a dense fluid. Rice and Kirkwood[16] have developed a small step diffusion model and Gray[17] has developed a configurational relaxation time model to describe these processes. Both of these approaches are in fairly good agreement with each other. They predict transport coefficients in fair agreement with experiment. Again, the comparison of theory with experiment suffers from a lack of precise equilibrium pair correlation functions. It is possible to extend the small step diffusion model somewhat further than has been done in the past, since quantities such as the mean square force on a particle are now available from measurements of isotope separation factors.[18-20] Thus, knowledge of the pair correlation function

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16. S. A. Rice, J. Kirkwood, J. Chem. Phys. 31, 901 (1959).

17. P. Gray, Mol. Phys. 7, 235 (1964).

18. G. Boato, G. Casanova, and A. Levi, J. Chem. Phys. 37, 201 (1962).

19. G. Boato, G. Casanova, and A. Levi, J. Chem. Phys. 60, 44 (1963).

20. G. Boato, G. Casanova, and A. Levi. J. Chem. Phys. (to be published).

may be completely circumvented. Furthermore, one may now avoid the very tenuous assumption first made by Rice and Kirkwood that the pair diffusion tensor is equal to twice the singlet diffusion tensor. It is also possible to use this model to calculate the transport coefficients for a liquid which has the idealized potential used in the Rice-Allnatt theory.

The objectives of this thesis are: 1) to extend and comment upon the small step diffusion model of Rice and Kirkwood, 2) to apply the Rice-Allnatt theory to fused salt systems, 3) to consider the possibility of casting the Rice-Allnatt theory into a Fokker-Planck representation, and 4) to explain the recent computer experiment by Rahman on Argon by an appeal to a non-Markovian theory for the regression of fluctuations.

CHAPTER I

THE MODIFIED RICE--ALLNATT EQUATION

1. Introduction

A theory of transport processes in liquids systematically developed from the Liouville equations was first formulated by Kirkwood.[5] The fundamental assumption of this theory is that, while the phase of a small number of molecules is, in general, a complex random process, the phase, or a function of it, can be treated as a simple Markov process if it is smoothed over a certain time interval τ .

The physical properties of gases are such that molecules can be said to undergo collisions with other molecules, and that between collisions they move freely. If a time can be chosen in such a way that it is long compared to the duration of a collision, but much shorter than the average time between collisions, then the random process can be treated in the binary collision approximation, and the Boltzmann equation is retrieved.[21] This approximation is best when the gas is dilute. When the gas is so dense that the probability of three or more molecules interacting during the interval becomes significant,[22]

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21. J. G. Kirkwood, J. Chem. Phys. 15, 72 (1947).

22. S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases (Cambridge University Press, Cambridge, England, 1939).

then corrections to the equation must be found; only in the case of a fluid of rigid spheres is the binary collision approximation rigorously correct for all densities, because the duration of a collision is vanishingly small.[23]

On the other hand, the liquid state is such that every molecule is continuously interacting with several others. In this case it was assumed that the momentum changes were small and frequent, so that the molecules could be said to behave as Browian particles to a first approximation, their phase distribution functions satisfying Fokker-Planck equations. This approximation has often been criticized on the grounds that it restricts the possible interactions to those involving small momentum transfer, while it is known that molecules must undergo large momentum changes during the frequent interactions in which they approach closer than the minimum of the pair potential well.

In a recent development of the theory of liquids, Rice and Allnatt[9,10] have described a model in which the pair potential is idealized as a hard core with a superimposed soft potential. The statistical features of the interactions are separated into binary hard core collisions, treated by means of a modified Boltzmann collision integral, and soft forces which are assumed to produce a quasi-Brownian motion. The numerical calculations of transport coefficients which have been made for this model are within a few percent of experiment, whereas those made with

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23. S. A. Rice, J. Kirkwood, J. Ross, and R. W. Zwanzig, J. Chem. Phys. 31, 575 (1959).

a pure Fokker-Planck equation only reproduce experimental data within a factor of 2. The Rice-Allnatt model, therefore, appears to give a fairly accurate picture of molecular interactions in a liquid.

In this chapter we attempt to throw light on the precise way in which the Rice-Allnatt theory is superior to the simple Fokker-Planck approach. In Section 2 of this chapter we show that the assumption of Brownian motion in the Kirkwood theory is too strong a statement of the mathematical approximations made. In fact, the Boltzmann collision integral can be replaced by a Fokker-Planck operator in a dilute gas. Thus, the Fokker-Planck operator can describe the large momentum transfers occurring during collisions in a gas, and the question arises as to why it cannot also do this for a liquid.

The effect of the hard-core collisions in the Rice-Allnatt model is to introduce a modified collision term such as that which appears in the Chapman-Enskog description of a dense gas. This can be separated into a term formally identical with the Boltzmann collision integral for a dilute gas, and a correction term, which represents the effect of local inhomogeneties in the density. In Section 3 of this chapter we assume that the pure Boltzmann term in the Rice-Allnatt equation can again be replaced by a Fokker-Planck operator with an effective friction coefficient ζ_H, which then combines additively with the soft friction coefficient ζ_S. The kinetic transport coefficients are calculated from the modified Rice-Allnatt equation, and compared with the results obtained from the original equation. It is concluded that the Fokker-Planck equation can describe not only the soft rapidly fluctuating forces, but also hard core binary collisions of a grazing character. It cannot, however, describe the head-on collisions which predominate when the system is so dense that grazing collisions are inhibited, and which are accounted for by the correction term.

2. Relation Between the Fokker-Planck Operator and the Boltzmann Collision Integral

The Fokker-Planck equation for the distribution function f for the phase ($\underline{r},\underline{p}$) of a particle is

$$\frac{\partial f}{\partial t} + m^{-1}\underline{p}\cdot\nabla_r f + \underline{X}\cdot\nabla_p f = \zeta\nabla_p\cdot\left[(m^{-1}\underline{p}-\underline{u})f + kT\nabla_p f\right], \tag{1}$$

where $\underline{X}$ is the average force to which the particle is subjected, $\underline{u}$ is the average velocity at $\underline{r}$, and ζ is the friction coefficient. In order to discuss the case of a dilute gas, we first review the conditions under which Eq. (1) is valid. We sometimes find it convenient to refer to the phase ($\underline{r},\underline{p}$) as a (multidimensional) random variable, which is its general meaning in the theory of random processes.

Prior to the development of the theory of liquids by Kirkwood, Eq. (1) was derived by considering a model of the Brownian motion of colloidal particles. In order to derive the equation it is necessary to assume that (a) the randomizing mechanism (fluctuating force acting on the particle) is not affected by the value of the random variable (and hence the random variable is a Markov process), (b) the time scales of the correlation of the fluctuating force and of the momentum, τ_F and m/ζ, respectively, are so widely separated that a time τ can be chosen such that

$$\tau_F << \tau << m/\zeta$$

and (c) the average force is a sufficiently slowly varying function of position that the particle does not experience significant changes in it during τ. If the fluctuating force is a stationary process, then the changes of the random variable may be written

$$\begin{aligned} \langle \Delta \underset{\sim}{p} \rangle^1 &= -\frac{1}{m}\zeta \underset{\sim}{p}\tau + O(\tau^2) \\ \langle \Delta \underset{\sim}{p} \Delta \underset{\sim}{p} \rangle^1 &= 3\zeta kT\tau \mathcal{E} + O(\tau^2);\ (\mathcal{E})_{ij} = \delta_{ij} \\ \langle \Delta \underset{\sim}{r} \rangle^1 &= \frac{1}{m}\underset{\sim}{p}\tau + O(\tau^2) \end{aligned} \tag{2}$$

with no explicit dependence on the time, but only on the length of the interval τ. The superscript 1 denotes the partial ensemble average; the particle has the same initial phase in each member of the ensemble. Terms in higher powers of τ than one are small if $\frac{\zeta}{m}\tau << 1$, i.e., subject to (b) above.

These are well-known features of the theory of Brownian motion, and we mention them here in detail because they are all true of Kirkwood's theory of liquids. However, the derivation of Eq. (1) in the latter theory is made from the Liouville equation, and the assumption that the processes are Markovian is made at a late stage, and not as a starting point. Consequently, we are able to analyze further the nature and validity of the assumptions than is possible in the former case.

The process of obtaining equations satisfied by the one- and two-molecule distribution functions may briefly be described in the following way: The distribution function for the isolated N-molecule system satisfies the Liouville equation, and, because of the equations of motion of classical mechanics, the phase of the system at any time is uniquely determined by the phase of the system at any other time. Thus the random variable $(\underline{r}_1, \underline{r}_2, \ldots., \underline{r}_N, \underline{p}_1, \underline{p}_2, \ldots., \underline{p}_N)$ (the phase of the whole system) is a simple kind of Markov process, and in general, the projections of this variable onto the subspaces of one and two molecules $(\underline{r}_1, \underline{p}_1)$ and $(\underline{r}_1, \underline{r}_2, \underline{p}_1, \underline{p}_2)$, respectively, are much more complicated processes than Markovian. Kirkwood's postulate was essentially that a time interval τ existed satisfying (b) above, over which these variables, or functions of them, could be smoothed or coarse grained, such that the new variables, or functions, would be Markovian.

In the course of the analysis, one obtains the now well-known expression for the friction coefficient

$$\zeta = \frac{1}{3kT\tau} \int_0^{\tau} ds \int_0^{\tau} ds' \langle \underset{\sim}{F}_1(t) \cdot \underset{\sim}{F}_1(t+s') \rangle' \qquad (3)$$

$\underset{\sim}{F}_1(t)$ is the instantaneous total force on Molecule 1 at a time t, so that the integrand is the time correlation function of the force

$$\langle \underset{\sim}{F}_1(t) \cdot \underset{\sim}{F}_1(t+s) \rangle' =$$

$$\int\int \prod_{i=2}^{N} d\underset{\sim}{r}_i d\underset{\sim}{p}_i f_1^{(1/N-1)} \underset{\sim}{F}_1(\underset{\sim}{R}) \cdot \underset{\sim}{F}_1(\underset{\sim}{R}_{s'}),$$

where $f^{(1/N-1)}$ is the distribution function of all the other molecules conditional on the fixed initial phase of molecule 1. $\underset{\sim}{R}$ denotes the position vectors of all molecules at time t, and with subscript s' at time s' later.

In order to carry through the derivation it is necessary to assume that the environment of the molecule, or pair of molecules, is in a stationary condition, i.e., that $f^{(1/N-1)}$ is independent of t. One should, therefore, have, for example,

$$\langle \underset{\sim}{F}_1(t) \cdot \underset{\sim}{F}_1(t+s) \rangle', \qquad \langle \underset{\sim}{p}_1(t) \cdot \underset{\sim}{p}_1(t+s) \rangle$$

independent of t, that is

$$\frac{\partial}{\partial t} \langle \underset{\sim}{p}_1(t) \cdot \underset{\sim}{p}_1(t+s) \rangle \equiv 0 \tag{4}$$

$$\frac{\partial}{\partial t} \langle \underset{\sim}{F}_1(t) \cdot \underset{\sim}{F}_1(t+s) \rangle \equiv 0 \tag{5}$$

Performing the differentiation in Eq. (4) explicitly, we have, using the notation $\dot{\underset{\sim}{p}}_1(t) = \frac{d\underset{\sim}{p}_1}{dt} = \underset{\sim}{F}_1(t)$, where F_1 is the force acting on particle

$$\frac{\partial}{\partial t} \langle \underset{\sim}{p}_1(t) \cdot \underset{\sim}{p}_1(t+s) \rangle = \langle \dot{\underset{\sim}{p}}_1(t) \cdot \underset{\sim}{p}_1(t+s) \rangle + \langle \underset{\sim}{p}_1(t) \cdot \dot{\underset{\sim}{p}}_1(t+s) \rangle \equiv 0 \tag{6}$$

For s = 0, Eq. (6) becomes

$$\begin{aligned} &\langle \dot{\underset{\sim}{p}}_1(t) \cdot \underset{\sim}{p}_1(t+s) \rangle + \langle \underset{\sim}{p}_1(t) \cdot \dot{\underset{\sim}{p}}_1(t+s) \rangle \\ &\qquad = 2 \langle \underset{\sim}{p}_1(t) \cdot \underset{\sim}{F}_1(t) \rangle = 0 \end{aligned} \tag{7}$$

Differentiating Eq. (6) w.r.t. t for a second time yields

$$\frac{\partial^2}{\partial t^2}\langle \underset{\sim}{p}_1(t)\cdot \underset{\sim}{p}_1(t+s)\rangle = \langle \ddot{\underset{\sim}{p}}_1(t)\cdot \underset{\sim}{p}_1(t+s)\rangle + \langle \underset{\sim}{p}_1(t)\cdot \ddot{\underset{\sim}{p}}_1(t+s)\rangle$$

$$+\ 2\langle \dot{\underset{\sim}{p}}_1(t)\cdot \dot{\underset{\sim}{p}}_1(t+s)\rangle \equiv 0 \tag{8}$$

or

$$\langle \ddot{\underset{\sim}{p}}_1(t)\cdot \underset{\sim}{p}_1(t+s)\rangle + \langle \underset{\sim}{p}_1(t)\cdot \ddot{\underset{\sim}{p}}_1(t+s)\rangle = -2\langle \underset{\sim}{F}_1(t)\cdot \underset{\sim}{F}_1(t+s)\rangle \tag{9}$$

In a stationary system it can be proved that a fixed ensemble average of a random variable $\underset{\sim}{p}_1$ must have the following property.

$$\langle \underset{\sim}{p}_1(t+s)\rangle' = \langle \underset{\sim}{p}_1(t-s)\rangle' \tag{10}$$

That is the momentum correlation function must be an even function of time. Furthermore, since the momentum correlation function in a stationary ensemble is independent of the origin of time, by definition, we can shift the origin of time from t to t-s, and get

$$\langle \underset{\sim}{p}_1(t)\cdot \ddot{\underset{\sim}{p}}_1(t+s)\rangle = \langle \underset{\sim}{p}_1(t-s)\cdot \ddot{\underset{\sim}{p}}_1(t)\rangle. \tag{11}$$

Substituting Eqs. (10) and (11) into (9) it is found that

$$2\langle \underline{p}_1(t)\cdot \ddot{\underline{p}}_1(t+s)\rangle = -2\langle \underline{F}_1(t)\cdot \underline{F}_1(t+s)\rangle \tag{12}$$

The identity $\frac{\partial}{\partial t}\,\underline{p}_1(t + s) = \frac{\partial}{\partial s}\,\underline{p}_1(t + s)$ may be substituted in Eq. (12), yielding the result

$$\frac{\partial^2}{\partial s^2}\langle \underline{p}_1(t)\cdot \underline{p}_1(t+s)\rangle = -\langle \underline{F}_1(t)\cdot \underline{F}_1(t+s)\rangle \tag{13}$$

Perhaps a more explicit derivation of Eq. (13) may be achieved through a discussion of the Liouville equation. As is well known, Liouville's theorem states that the N-particle distribution function $f^{(N)}$ obeys a continuity equation in the complete phase space of the system.

$$i\,\frac{\partial f^{(N)}}{\partial t} + L f^{(N)} = 0$$

where

$$L = i \sum_{i=1}^{N} \left\{ \frac{\underline{p}_i}{m_i}\cdot \nabla_{R_i} + \underline{F}_i \cdot \nabla_{p_i} \right\} \tag{14}$$

m_i is the mass, and $\underline{F}_i$ is the total force acting on particle i when it is at position $\underline{R}_i$, moving with momentum $\underline{p}_i$. The factor i is introduced to make the operator L self-adjoint. This last property is well known. We operate on $\underline{P}_1(t)$ with L to find that

$$L\,\underline{P}_1(t) = i\,\dot{\underline{P}}_1(t) \tag{15}$$

and

$$L^2\,\underline{P}_1(t) = -\,\ddot{\underline{P}}_1(t) \tag{16}$$

Thus

$$\langle \ddot{\underline{P}}_1(t)\cdot\underline{P}_1(t+s)\rangle = -\,\langle (L^2\,\underline{P}_1(t))\cdot\underline{P}_1(t+s)\rangle \tag{17}$$

and when the self-adjoint property of L is exploited it is found that

$$\langle \ddot{\underline{P}}_1(t)\cdot\underline{P}_1(t+s)\rangle = \langle \underline{P}_1(t)\cdot\ddot{\underline{P}}_1(t+s)\rangle \tag{18}$$

Thus Eq. (9) becomes, on insertion of Eq. (18)

$$\langle \underset{\sim}{P}_1(t) \cdot \ddot{\underset{\sim}{P}}_1(t+s) \rangle = - \langle \underset{\sim}{F}_1(t) \cdot \underset{\sim}{F}_1(t+s) \rangle \tag{12}$$

which is precisely Eq. (12) and Eq. (13) follows from this in the same way it did before.

From Eq. (12) another interesting relationship which will be used in the future may be found. When s = 0, Eq. (12) becomes

$$\begin{aligned} \langle \ddot{\underset{\sim}{P}}_1(t) \cdot \underset{\sim}{P}_1(t) \rangle &= - \langle \underset{\sim}{F}_1(t) \cdot \underset{\sim}{F}_1(t) \rangle \\ \ddot{\underset{\sim}{P}}_1(t) &= \frac{d}{dt} \underset{\sim}{F}_1(t) \equiv \left(\frac{\underset{\sim}{P}_1}{m} \cdot \nabla_{R_1} \right) \underset{\sim}{F}_1(t) \end{aligned} \tag{19}$$

This yields on insertion into Eq. (19)

$$\begin{aligned} - \langle \underset{\sim}{F}_1(t) \cdot \underset{\sim}{F}_1(t) \rangle &= \frac{1}{m} \langle \underset{\sim}{P}_1(t) \cdot \left(\underset{\sim}{P}_1(t) \cdot \nabla_{R_1} \right) \underset{\sim}{F}_1(t) \rangle \\ &= \frac{1}{m} \langle \left(\frac{\underset{\sim}{P}_1}{m} \cdot \nabla_{R_1} \right) \underset{\sim}{P}_1 \cdot \underset{\sim}{F}_1(t) \rangle \\ &= \frac{1}{m} \langle \underset{\sim}{P}_1(t) \underset{\sim}{P}_1(t) : \nabla_{R_1} \underset{\sim}{F}_1(t) \rangle \end{aligned} \tag{20}$$

Certain statements may be made about the right hand side of Eq. (20). This average may be written out in component form.

Here, let i and j each represent the three cartesian components of the vectors, then

$$\left\langle \underset{\sim}{P_1}(t)\underset{\sim}{P_1}(t) : \nabla_{R_1} \underset{\sim}{F_1}(t) \right\rangle = \left\langle \sum_{i=1}^{3}\sum_{j=1}^{3} P_{1i}(t) P_{1j}(t) \frac{\partial}{\partial x_{1j}} F_{1i}(t) \right\rangle$$

$$= \sum_{i=1}^{3}\sum_{j=1}^{3} \left\langle P_{1i}(t) P_{1j}(t) \frac{\partial}{\partial x_{1j}} F_{1i}(t) \right\rangle \tag{21}$$

The brackets indicate an equilibrium ensemble average. All terms which have $i \neq j$ disappear as the integrand in the ensemble average of the momenta then becomes odd. Also, since the particular systems with which we shall deal are isotropic, the $i \neq j$ terms for the gradient will vanish. Thus Eq. (21) becomes

$$\left\langle \underset{\sim}{P_1}(t)\underset{\sim}{P_1}(t) : \nabla_{R_1} \underset{\sim}{F_1}(t) \right\rangle = \left\langle \left(\underset{\sim}{P_1}(t)\cdot \underset{\sim}{P_1}(t)\right) \nabla_{R_1} \cdot \underset{\sim}{F_1}(t) \right\rangle \tag{22}$$

Furthermore, the configuration and momentum averages can be performed separately. From the equipartition of energy,

$$\left\langle \underset{\sim}{P_1}(t)\cdot \underset{\sim}{P_1}(t) \right\rangle = 3mKT$$

and

$$\left\langle P_{1j}(t) P_{1j}(t) \right\rangle = mKT$$

and from

$$\nabla_{R_1} \cdot \underset{\sim}{F_1}(t) = -\nabla_{R_1}^2 U$$

where U is the potential energy of particle 1 due to its interactions with its surrounding. Thus it is found that

$$\langle \underset{\sim}{F}_1(t)\cdot\underset{\sim}{F}_1(t)\rangle = KT\langle \nabla_{R_1}^2 U\rangle \tag{23}$$

In terms of the normalized momentum correlation function, defined by

$$\Psi(s) = \frac{1}{3mKT}\langle \underset{\sim}{P}_1(t)\cdot\underset{\sim}{P}_1(t+s)\rangle \quad , \quad \Psi(0)=1$$

Eq. (4) and (5) become

$$\begin{aligned}\dot{\Psi}(0) &= 0\\ \ddot{\Psi}(s) &= -\frac{1}{3mKT}\langle \underset{\sim}{F}_1(t)\cdot\underset{\sim}{F}_1(t+s)\rangle\end{aligned} \tag{24}$$

From Eq. (3) and (24), the expression for the friction coefficient now becomes after integration

$$\zeta/m = \frac{1-\Psi(\tau)}{\tau} \tag{25}$$

Clearly if one is to be able to obtain a friction coefficient independent of τ, then there must be a range of τ for which $\Psi(\tau) \sim 1 - \frac{\zeta}{m}\tau + O(\tau^2)$. In other words, one has again the conditions (b) and (c), namely

$$\Psi(\tau) = \exp[-(\zeta/m)\tau] \quad \text{if} \quad \tau_F \ll \tau \ll m/\zeta$$

The meaning of τ_F here is primarily the temporal extent of the flat top of $\Psi(\tau)$: τ_F represents the magnitude of times for which the motion of a molecule is coherent, i.e., predictable from a knowledge of its momentum, and the force on it, at time s = 0.

It is easy to see that Eq. (25) is just a restatement of Eq. (2). For example, we have

$$\langle \Delta \underset{\sim}{P}_1 \rangle' = \langle \underset{\sim}{P}_1(\tau) - \underset{\sim}{P}_1(0) \rangle' = \langle \underset{\sim}{P}_1(\tau) \rangle' - \underset{\sim}{P}_1(0)$$

$$= [\Psi(\tau) - 1]\, \underset{\sim}{P}_1(0) = -\frac{1}{m}\zeta \underset{\sim}{P}_1(0)\tau + O(\tau^2)$$

Eq. (2) states that the average increments in momentum in a short time τ must be proportional to τ. This is almost trivially true for colloidal particles, since these are so massive compared to the molecules with which they interact, that the behavior of individual particles is close to the average behavior. On the other hand, these relations should be satisfied for other systems provided that two time-scales can be identified, which differ by some orders of magnitude and possess similar physical significance.

As an example, consider the dilute gas. Here two widely different time scales are easily identified as the duration of a collision τ_c and the mean free time τ_f, so that an interval τ may be chosen to satisfy

$$\tau_c << \tau << \tau_f . \tag{26}$$

The duration of a collision τ_c may be interpreted in much the same way as τ_F; namely as a time in which the motion of a molecule is predictable from a knowledge of its initial momentum and the force on it at the initial instant. For times longer than τ_c, a second collision may occur, completely uncorrelated with the first, so that the extent of the flat top of Ψ will be defined by τ_c. At the other end of the scale the mean free time τ_f may be interpreted as the decay time of Ψ since the momentum after a second collision is almost uncorrelated with its initial value, except for a small persistence effect, and the free time has a probability distribution similar to that for free paths $\tau_f^{-1}\exp(-t/\tau_f)$.

Since the phase distribution function for the dilute gas satisfies the Boltzmann equation, the foregoing discussion indicates that the Fokker-Planck operator (the right hand member of Eq. (1)) is equivalent to the Boltzmann collision integral. We do not give a derivation of this equivalence here since it has been considered in detail elsewhere,[24,25] and explicit forms for the friction coefficient for a dilute gas have been given by O'Toole and Dahler.[26] It is sufficient to point out that both the Fokker-Planck and Boltzmann equations may be derived from the Markov integral equation by different treatments, but that this is not sufficient to establish their equivalence for a particular system; it is necessary first to establish the foregoing physical arguments.

It seems unlikely that conditions (b) and (c) are satisfied for a dense gas or liquid. There is evidence from the scattering of thermal neutrons[27] and from recent computer experiments[28] that Ψ has the form of damped oscillations. It will be seen in Chapter IV that this behavior can be accounted for by a non-Markovian theory for the regression of fluctuations. There is also evidence that oscillations occur in Ψ even in a rigid sphere fluid at sufficiently high densities.[29] On the other hand, there is no reason apparent at the present time why the influence of the soft N-body force cannot be regarded as leading to a quasi-Brownian motion; this only requires that Eq. (2) is satisfied by momentum increments due to the soft

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24. E. A. Desloge, Am. J. Phys. 31, 237 (1963).
25. J. Enoch, Phys. Sl.3, 353 (1960).
26. J. T. O'Toole and J. S. Dahler, J. Chem. Phys. 33, 1496 (1960).
27. P. Egelstaff, Advan. Phys. 11, 203 (1962).
28. A. Rahman, (private communication).
29. T. Wainwright and B. J. Alder, Nuovo Cimento Suppl. 9, 116 (1959).

force, and does not imply that the molecules are Brownian particles in any other sense.

The foregoing discussion of the equivalence of the Boltzmann collision integral to a Fokker-Planck operator under certain circumstances, can be interpreted as a statement of purely mathematical content. Thus, the properties of the Rice-Allnatt equation should differ from those of a Fokker-Planck equation only because it includes the contribution arising from the modified Boltzmann term due to inhomogeneities in density. We therefore propose to study the properties of the Rice-Allnatt equation by modifying it to a Fokker-Planck operator, with a friction coefficient combining the effects of the Boltzmann term and the original soft-force Fokker-Planck operator, and the correction term only.

3. Solution of the Modified Rice-Allnatt Equation

The modified Rice-Allnatt equation described in the previous section is

$$\mathcal{D}\bar{f}^{(1)} = J_2 + \zeta \mathcal{Q} \bar{f}^{(1)} \tag{27}$$

where

$$\mathcal{D}f^{(1)} = \frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{1}{m} \underset{\sim}{p_1} \cdot \nabla_{r_1} \bar{f}^{(1)} + \underset{\sim}{X}_1 \cdot \nabla_{p_1} \bar{f}^{(1)} \tag{28}$$

$$J_2 = g_0^{(2)}(\sigma) \iint \left[\bar{f}^{(1)}(\underset{\sim}{r}_1, \underset{\sim}{p}_1 - \Delta \underset{\sim}{p}_1; t)\, \sigma \underset{\sim}{k} \cdot \nabla_{r_1} \bar{f}^{(1)}(\underset{\sim}{r}_1, \underset{\sim}{p}_2 - \Delta \underset{\sim}{p}_2; t) + \bar{f}^{(1)}(\underset{\sim}{r}_1, \underset{\sim}{p}_1; t)\, \sigma \underset{\sim}{k} \cdot \nabla_{r_1} \bar{f}^{(1)}(\underset{\sim}{r}_1, \underset{\sim}{p}_2; t) \right] \left(\frac{p_{12}}{m} \right) b\,db\,d\varepsilon\,d\underset{\sim}{p}_2 \tag{29}$$

and

$$\mathcal{Q} \bar{f}^{(1)} = \nabla_{p_1} \cdot \left[(m^{-1} \underset{\sim}{p}_1 - \underset{\sim}{u}) \bar{f}^{(1)} + kT \nabla_{p_1} \bar{f}^{(1)} \right] \tag{30}$$

where $g_0^{(2)}(\sigma)$ is the equilibrium pair correlation function, σ, the diameter of the molecules, ζ, the total friction coefficient, $\underline{k}$, a unit vector which defines the position of molecule 2 with respect to molecule 1 at their distance of closest approach, b the impact parameter and azimuthal angle, ε, describing the scattering process, $\frac{1}{m}|p_{12}|$ the relative speed of particle 2 with respect to particle 1, and $\bar{f}^{(1)}$ the singlet distribution function. The pure Boltzmann collision integral, usually denoted by J_1, has been replaced by a Fokker-Planck operator, with friction coefficient

$$\zeta = \zeta_H + \zeta_S \tag{31}$$

where ζ_s is the soft friction coefficient of Rice and Allnatt.

To obtain a solution of Eq. (27), a perturbation procedure is used in conjunction with an expansion in terms of certain eigenfunctions of the Fokker-Planck operator. We write the phase distribution function of a single particle as the product of the zeroth order (local equilibrium) singlet distribution function and a perturbation, viz,

$$\bar{f}^{(1)}(1) = \bar{f}_0^{(1)}(1)\left(1 + \phi_1\right), \tag{32}$$

where $f_o^{(1)}(1)$ is the Maxwellian distribution, and ϕ_1 is the perturbation to this distribution;

$$\bar{f}_0^{(1)}(1) = \frac{(2\pi mKT)^{-3/2}}{v} \exp\left[-\left(\frac{1}{m}\underset{\sim}{p}_1 - \underset{\sim}{u}\right)^2 \frac{m}{2KT}\right] \tag{33}$$

If Eq. (32) is substituted into the left hand-side of Eq. (27) and the space gradients in ϕ_1 are neglected, we find, after using the hydrodynamic equations

$$\frac{\partial v}{\partial t} = v^2 \nabla_{r_1} \cdot (\underset{\sim}{u}/v) \tag{34}$$

$$\frac{\partial \underset{\sim}{u}}{\partial t} = -\underset{\sim}{u}\cdot\nabla_{r_1}\underline{u} - v\nabla_{r_1} p + \frac{1}{m}\underline{X}_1 \tag{35}$$

$$\frac{\partial T}{\partial t} = -\underset{\sim}{u}\cdot\nabla_{r_1} T - \frac{Tv}{C_v}\left(\frac{\partial p}{\partial T}\right)_\rho \nabla_{r_1}\cdot\underset{\sim}{u} \tag{36}$$

(which are obtained by multiplying Eq. (27) successively by m, $\underline{p}_1$, and $\frac{p_1^2}{2m}$ and integrating over the phase space of particle 1) to eliminate the space and time derivative of the volume per molecule v , the local hydrodynamic velocity $\underset{\sim}{u}$, and the local temperature T, that the streaming term is

$$\mathcal{D}\bar{f}_0^{(1)}(1)(1+\phi_1)$$

$$= \bar{f}_0^{(1)}(1)\left(\left\{2\underset{\approx}{b} + \left[\frac{v}{C_v}\left(\frac{\partial p}{\partial T}\right)_\rho - \frac{2}{3}\right]\left(\frac{3}{2} - W_1^2\right)\underline{\underline{U}}\right\}:\nabla_{r_1}\underline{u} \right. \tag{37}$$

$$\left. - \left(\frac{2KT}{m}\right)^{1/2}\left\{\frac{3}{2} + \alpha T - W_1^2\right\}\underline{W}_1\cdot\nabla_{r_1}\ln T\right)$$

where $\underline{W}_1 = \left(\frac{m}{2KT}\right)^{1/2}\left[\frac{1}{m}\underset{\sim}{p}_1 - \underset{\sim}{u}\right]$ is a dimensionless peculiar velocity and $\underset{\approx}{b} = \underline{W}_1\underline{W}_1 - \frac{1}{3}W_1^2$ is the traceless dyadic of $\underline{W}_1$. The quantity ρ is the mass density, $\frac{m}{v}$,

C_V is the specific heat at constant volume per molecule, and p the hydrostatic pressure. It must be added that the equations of change (34), (35), and (36) are derived by considering the distribution function to be Maxwellian. This is the procedure used in the Chapman-Enskog solution of the Boltzmann equation.[22] The term J_2 in Eq. (37), which we shall henceforth call the excluded volume term, may be handled in the steady-state approximation by analyzing the hard core dynamics in detail. We omit the details of our calculation, and merely indicate where they can be found.[10]

$$J_2 = \bar{f}_0^{(1)}(1)\, g_0^{(2)}(\sigma)\Big\{\left(\frac{2\pi\sigma^3}{15v}\right)\left(\frac{2KT}{m}\right)^{1/2}\left(-\frac{5}{2}+10\alpha T-3W_1^2\right)\underset{\sim}{W}_1\cdot\nabla_{r_1}\ln T$$
$$-\left(\frac{4\pi\sigma^3}{3v}\right)\left[\frac{1}{3}\left(\frac{3}{2}-W_1^2\right)\underset{\approx}{U}-\frac{2}{5}\underset{\approx}{b}\right]:\nabla_{r_1}\underset{\sim}{u}\Big\} \tag{38}$$

The streaming term and the excluded volume term in the final equation may now be combined

$$\left[g_0^{(2)}(\sigma)\right]^{-1}(\zeta_H+\zeta_S)\nabla_{p_1}\cdot\Big[\left(\frac{1}{m}\underset{\sim}{p}_1-\underset{\sim}{u}\right)\bar{f}^{(1)}(1)$$
$$+KT\nabla_{p_1}\bar{f}^{(1)}(1)\Big] = \underset{\sim}{K}\cdot\nabla_{r_1}\ln T+\underset{\approx}{L}:\nabla_{r_1}\underset{\sim}{u} \tag{39}$$

where

$$K = -\bar{f}_0^{(1)}(1)\left(\frac{2KT}{m}\right)^{1/2}\left[\frac{1}{g_0^{(2)}(\sigma)}\left(\frac{3}{2}+\alpha T - W_1^2\right)\underset{\sim}{W}_1 \right. \tag{40}$$

$$\left. +\left(\frac{2\pi\sigma^3}{15v}\right)\left(-\frac{5}{2}+10\alpha T-3W_1^2\right)\underset{\sim}{W}_1\right]$$

and

$$\underset{\approx}{L} = \bar{f}_0^{(1)}(1)\left(\frac{1}{g_0^{(2)}(\sigma)}\left\{2\underset{\approx}{b}+\left[\frac{v}{C_v}\left(\frac{\partial p}{\partial T}\right)_\rho-\frac{2}{3}\right]\left(\frac{3}{2}-W_1^2\right)\underset{\approx}{U}\right\}\right. \tag{41}$$

$$\left.-\left(\frac{4\pi\sigma^3}{3v}\right)\left[\frac{1}{3}\left(\frac{3}{2}-W_1^2\right)\underset{\approx}{U}-\frac{2}{5}\underset{\approx}{b}\right]\right)$$

The equation can be rewritten in the following form after first transforming from $\underset{\sim}{P}_1$ to $\underset{\sim}{W}_1$ on the left-hand side,

$$B\nabla_{W_1}\cdot\left[\exp(-W_1^2)\nabla_{W_1}\phi_1\right] = \underset{\sim}{K}'\cdot\nabla_{r_1}\ln T \tag{42}$$

$$+\underset{\approx}{L}':\nabla_{r_1}\underset{\sim}{u}$$

where

$$B = \left[(\zeta_H+\zeta_S)/g_0^{(2)}(\sigma)\,(8mkT)^{1/2}\right] \tag{43}$$

and

$$\underset{\sim}{K}' = \underset{\sim}{K}\, v\, (2\pi m k T)^{3/2} \tag{44}$$

and

$$\underset{\approx}{L}' = \underset{\approx}{L}\, v\, (2\pi m k T)^{3/2} (m/2kT)^{1/2} \tag{45}$$

From the linear form of Eq. (22), it is seen that the perturbation function can only depend upon the temperature gradient and the velocity flow gradient. This suggests the form of the solution to be

$$\phi_1 = \underset{\sim}{A}_1 \cdot \nabla_{r_1} \ln T + \underset{\approx}{B}_1 : \nabla_{r_1} \underset{\sim}{u} \tag{46}$$

The Auxiliary conditions

$$\int \bar{f}_0^{(1)}(1)\, \phi_1\, d\underset{\sim}{p}_1 = 0, \tag{47}$$

$$\int \bar{f}_0^{(1)}(1)\, \phi_1 \left[\frac{1}{m}\underset{\sim}{p}_1 - \underset{\sim}{u}\right] d\underset{\sim}{p}_1 = 0 \tag{48}$$

$$\int \bar{f}_0^{(1)}(1)\, \phi_1 \left[\frac{1}{m}\underset{\sim}{p}_1 - \underset{\sim}{u}\right]^2 d\underset{\sim}{p}_1 = 0 \tag{49}$$

are imposed on the perturbation function to insure that v, $\underset{\sim}{u}$, and T are the local thermodynamic variables. The functions $\underset{\sim}{K}$ and $\underset{\approx}{L}$ in Eqs. (40) and (41) are the same as those that appear in the Chapman and Enskog theory of the dense gas. There is a theorem due to Hilbert[30] that the inhomogeneities in a Fredholm integral equation must, when multiplied by the solutions of the associated homogeneous integral equation and integrated over the argument, give zero. Thus, since mass, momentum, and energy are the solutions of the associated homogeneous equation for the dense gas, we have the following ten conditions on $\underset{\sim}{K}$ and $\underset{\approx}{L}$:

$$\int M\, d\underset{\sim}{p}_1 = 0$$

$$\int M \left[\frac{1}{m}\underset{\sim}{p}_1 - \underset{\sim}{u}\right] d\underset{\sim}{p}_1 = 0$$

$$\int M \left[\frac{1}{m}\underset{\sim}{p}_1 - \underset{\sim}{u}\right]^2 d\underset{\sim}{p}_1 = 0$$

where $M = \underset{\sim}{K}$ or $\underset{\approx}{L}$.

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30. See, for example, R. Courant and D. Hilbert, Methods of Mathematical Physics (Interscience Publishers, Inc., New York, 1954), Vol. I.

Our inhomogeneities conform to these conditions. Equation (42) may now be separated into

$$\beta \nabla_{W_1} \cdot [\exp(-W_1^2) \nabla_{W_1} \underset{\sim}{A}_1] = \underset{\sim}{K}' \tag{50}$$

and

$$\beta \nabla_{W_1} \cdot [\exp(-W_1^2) \nabla_{W_1} \underset{\approx}{B}_1] = \underset{\approx}{L}' \tag{51}$$

Equation (51) can further be separated into

$$\underset{\approx}{L}' = \underset{\approx}{L}^{(1)'} + L^{(2)'} \underset{\approx}{U} \tag{52}$$

where

$$L^{(1)'} = [2/g_0^{(2)}(\sigma)](1 + \tfrac{1}{5}C)\exp(-W_1^2)\,\underset{\approx}{b}\,, \tag{53}$$

and

$$L^{(2)'} = [D/g_0^{(2)}(\sigma)]\exp(-W_1^2)(\tfrac{3}{2} - W_1^2). \tag{54}$$

In Eqs. (53) and (54),

$$C = g_0^{(2)}(\sigma)\left(\frac{4\pi\sigma^3}{3v}\right) \tag{55}$$

and

$$D = \left(\frac{v}{C_v}\right)\left(\frac{\partial p}{\partial T}\right)_\rho - \frac{2}{3} - \frac{1}{3}C \tag{56}$$

Thus $\underline{\underline{B}}_1$ may be separated as

$$\underline{\underline{B}}_1 = \underline{\underline{B}}_1^{(1)} + B_1^{(2)}\underline{\underline{U}} \tag{57}$$

and Eq. (51) becomes

$$B\nabla_{W_1}\cdot\left[\exp(-W_1^2)\nabla_{W_1}\underline{\underline{B}}_1^{(1)}\right] = \underline{\underline{L}}^{(1)\prime} \tag{58}$$

and

$$B\nabla_{W_1}\cdot\left[\exp(-W_1^2)\nabla_{W_1}B_1^{(2)}\right] = L^{(2)\prime} \tag{59}$$

The inhomogeneities $\underline{K}'$, $\underline{\underline{L}}^{(1)\prime}$, $L^{(2)\prime}$, may be expressed in terms of the Sonine polynomials in W_1^2, $S_{3/2}^{(m)}$, $S_{5/2}^{(m)}$, and $S_{1/2}^{(m)}$, respectively, as

$$\underline{K}' = -[\exp(-W_1^2)/g_0^{(2)}(\sigma)]\left[(10C'+1)(\alpha T-1)S_{3/2}^{(0)} + (3C'+1)S_{3/2}^{(1)}\right]\underline{W}_1 \tag{60}$$

$$\underline{\underline{L}}^{(1)'} = \underline{E}\exp(-W_1^2)S_{5/2}^{(0)}\,\underline{\underline{b}}\,, \tag{61}$$

and

$$L^{(2)'} = [D/g_0^{(2)}(\sigma)]\exp(-W_1^2)S_{1/2}^{(1)} \tag{62}$$

where

$$C' = g_0^{(2)}(\sigma)\left(\frac{2\pi\sigma^3}{15v}\right) = \frac{1}{10}C$$
$$\underline{E} = 2\left(1+\frac{1}{5}C\right)/g_0^{(2)}(\sigma) \tag{63}$$

where

$$S_n^{(m)}(x) = \sum_j \frac{(-1)^j (m+n)!}{(n+j)!(m-j)!j!} x^j$$

Now it may be shown that the polynomials $S_{3/2}^{(m)}\underline{W}_1$, $S_{5/2}^{(m)}\underline{\underline{b}}$, and $S_{1/2}^{(m)}$ are, when multiplied by $\exp(-W_1^2)$, eigenfunctions of the Fokker-Planck operator, with eigenvalues $-2(2m+1)$, $-4(m+1)$, and $-4m$, respectively, so that $\underline{A}_1$, $\underline{\underline{B}}_1^{(1)}$, and $B_1^{(2)}$, may be expressed in terms of these polynomials only. Thus

$$\underline{A}_1 = \underline{W}_1 \sum_{m=1}^{\infty} a_m S_{3/2}^{(m)}(W_1^2) \tag{64}$$

$$\underline{\underline{B}}_1^{(1)} = \underline{\underline{b}} \sum_{m=0}^{\infty} b_m^{(1)} S_{5/2}^{(m)}(W_1^2) \tag{65}$$

and

$$B_1^{(2)} = \sum_{m=2}^{\infty} b_m^{(2)} S_{1/2}^{(m)}(W_1^2) \tag{66}$$

The relations (46), (47) and (48) impose conditions upon these series which they must satisfy before being inserted in Eqs. (50), (58) and (59). Inspection shows that $\underline{A}_1$ is affected by Eq. (47), $B_1^{(2)}$ by Eqs. (46) and (48) and $\underline{\underline{B}}_1^{(1)}$ is unaffected. Thus we find $a_o = 0$ and $b_o^{(2)} = b_1^{(2)} = 0$. Use of the orthogonality and recursion relations for the Sonine polynomials then leads to

$$a_1 = \frac{15}{4}\left(\frac{2KT}{m}\right)^{1/2} \frac{[v/g_o^{(2)}(\sigma)] + \frac{2}{5}\pi\sigma^3}{16\Omega^{(2,2)} + [45\zeta_s v/4mg_o^{(2)}(\sigma)]} \tag{67}$$

$$a_n = 0, \qquad n > 1$$

$$b_o^{(1)} = -5\,\frac{[v/g_o^{(2)}(\sigma)] + \frac{4}{15}\pi\sigma^3}{\frac{20}{3}\Omega^{(2,2)} + [5\zeta_s v/mg_o^{(2)}(\sigma)]} \tag{68}$$

$$b_n^{(1)} = 0, \qquad n > 1$$

and

$$b_n^{(2)} = 0, \qquad n > 1 \tag{69}$$

ζ_H is given by

$$\zeta_H = 4\Omega^{(2,2)}\left[m g_0^{(2)}(\sigma)/3v \right] \tag{70}$$

where $\Omega^{(2,2)}$ is the reduced hard-core cross section. (This is the value derived by Chapman and Cowling for isothermal tracer diffusion).

The solution in the linear approximation may now be obtained from Eqs. (32), (33), (42)-(46), and (64)-(69); we do not write it here.

4. Evaluation of the Transport Coefficients

In this section the kinetic and the collisional transport components of the shear viscosity and thermal conductance are calculated. The starting point for this calculation is the work of Irving and Kirkwood[31] who derived expressions for the stress tensor and the heat flux by identifying observable fluxes with the ensemble average of the corresponding microscopic fluxes. Their results are

$$\underline{\underline{\sigma}}_K = -\sum_{k=1}^{N} m\langle (m^{-1}\underline{p}_k - \underline{u})(m^{-1}\underline{p}_k - \underline{u})\delta(\underline{r}_k - \underline{x}_1); f^{(N)} \rangle, \tag{71}$$

31. J. H. Irving and J. G. Kirkwood, J. Chem. Phys. 18, 817 (1950).

$$\underset{\approx}{\sigma}_v = -\frac{1}{2}\int \underset{\sim}{r}\,\nabla_r V \Big\langle \sum_{j\neq k=1}^{N} \delta(\underset{\sim}{r}_j - \underset{\sim}{r})\,\delta(\underset{\sim}{r}_k - \underset{\sim}{x}_1 - \underset{\sim}{r});\, f^{(N)} \Big\rangle d\underset{\sim}{r}, \tag{72}$$

$$\underset{\sim}{q}_K = \sum_{k=1}^{N} \Big\langle \tfrac{1}{2} m \,|m^{-1}\underset{\sim}{p}_k - \underset{\sim}{u}|^2 (m^{-1}\underset{\sim}{p}_k - \underset{\sim}{u})\,\delta(\underset{\sim}{r}_k - \underset{\sim}{x}_1);\, f^{(N)} \Big\rangle, \tag{73}$$

$$\begin{aligned}\underset{\sim}{q}_v &= \frac{1}{2}\int [V \underset{=}{U} - \underset{\sim}{r}\nabla_r V]\cdot \Big\langle \sum_{j\neq k=1}^{N} (m^{-1}\underset{\sim}{p}_k - \underset{\sim}{u})\,\delta(\underset{\sim}{r}_j - \underset{\sim}{r}) \\ &\quad \times \delta(\underset{\sim}{r}_k - \underset{\sim}{x}_1 - \underset{\sim}{r});\, f^{(N)} \Big\rangle d\underset{\sim}{r},\end{aligned} \tag{74}$$

where

$$\langle \alpha; f^{(N)} \rangle = \int \cdots \int \alpha(\underset{\sim}{R}, \underset{\sim}{P}) f^{(N)}(\underset{\sim}{R}, \underset{\sim}{P})\, d\underset{\sim}{R}\, d\underset{\sim}{P},$$

$$\underset{\sim}{u} = \Big\langle \sum_{k=1}^{N} \delta(\underset{\sim}{r}_k - \underset{\sim}{x}_1);\, f^{(N)} \Big\rangle^{-1} \Big\langle \sum_{k=1}^{N} m^{-1}\underset{\sim}{p}_k\,\delta(\underset{\sim}{r}_k - \underset{\sim}{x}_1);\, f^{(N)} \Big\rangle, \tag{75}$$

and $\underset{\sim}{x}_1$ is the position of a field point in the fluid, $\underset{\sim}{\sigma}_K$, and $\underset{=}{\sigma}_v$ are the kinetic and intermolecular force parts of the stress tensor and $\underset{\sim}{q}_K$ and $\underset{\sim}{q}_v$ are the corresponding parts of the heat flux. Integration of these expressions reduces them to the point where only the pair distribution function appears. The pair distribution function may then be related to the singlet distribution functions

$$f^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{p}_1, \underset{\sim}{p}_2) = g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{p}_1, \underset{\sim}{p}_2)\, f^{(1)}(\underset{\sim}{r}_1, \underset{\sim}{p}_1)\, f^{(1)}(\underset{\sim}{r}_2, \underset{\sim}{p}_2), \tag{76}$$

Consistent with our derivation we denote $g_o^{(2)}$ evaluated at $\underset{\sim}{R}_2 - \underset{\sim}{R}_1 = \sigma \underset{\sim}{k}$ in Eq. (56) as $g_o^{(2)}(\sigma)$. The resulting fluxes are, after the binary dynamics are analyzed,

$$\underset{\approx}{\sigma}_K = -m \iiint \bar{f}^{(1)}(1)(m^{-1}\underset{\sim}{p}_1 - \underset{\sim}{u})(m^{-1}\underset{\sim}{p}_1 - \underset{\sim}{u})\, d^3 p_1 \tag{77}$$

$$\underset{\approx}{\sigma}_v = \frac{2N(N-1)\, g_o^{(2)}(\sigma)}{m} \int \cdots \int \underset{\sim}{k}\underset{\sim}{k}\, (\underset{\sim}{p}_{12} \cdot \underset{\sim}{k})\, \bar{f}^{(1)}(1)\, \bar{f}^{(1)}(2)\, |\underset{\sim}{p}_{12}|\, b\, db\, d\varepsilon\, d\underset{\sim}{p}_1\, d\underset{\sim}{p}_2 \tag{78}$$

$$\underset{\sim}{q}_k = \frac{m}{2} \iiint \bar{f}^{(1)}(1)\, |m^{-1}\underset{\sim}{p}_1 - \underset{\sim}{u}|^2 (m^{-1}\underset{\sim}{p}_1 - \underset{\sim}{u})\, d^3 p_1 \tag{79}$$

$$\underset{\sim}{q}_v = - \frac{N(N-1)\sigma g_0^{(2)}(\sigma)}{m^2} \int \cdots \int \underline{K}(\underline{K} \cdot \underline{P}_{12}) \underline{K} \cdot (\underline{P}_1 + \underline{P}_2) \times \bar{f}^{(1)}(1) f^{(1)}(2) |\underline{P}_{12}| b\,db\,d\varepsilon\,d\underline{P}_1\,d\underline{P}_2 \qquad (80)$$

It must be remembered that the only intermolecular force contribution to the fluxes that is being calculated is that due to the infinitely repulsive hard core. The solution obtained in the previous section for Eq. (32) is used in these expressions and the results are compared with the linear phenomenological laws

$$\underset{\approx}{\sigma} = - \left[p + \left(\tfrac{2}{3}\eta - \varphi \right) \nabla_r \cdot \underset{\sim}{u} \right] \underset{\approx}{U} + 2\eta \underset{\approx}{\varepsilon} \qquad (81)$$

and

$$\underset{\sim}{q} = - \kappa \, \nabla_r T \qquad (82)$$

where p is the hydrostatic pressure, η the shear viscosity, φ the bulk viscosity, $\underset{\approx}{\varepsilon}$ the symmetrized rate of strain tensor, and κ the thermal conductivity. By comparing the microscopic fluxes calculated above with (81) and (82) the transport coefficients may be identified. We represent the kinetic part by a subscript k and the hard core part by a subscript σ.

The transport coefficients are written in terms of the coefficienct which appear in the perturbation to the Maxwellian distribution

$$\phi_1 = \underset{\sim}{A}_1 \cdot \nabla_{r_1} \ln T + \underline{\underline{B}}_1 : \nabla_{r_1} \underset{\sim}{u} = a_1 S^{(1)}_{3/2}(w_1^2) \underset{\sim}{W}_1 \cdot \nabla_{r_1} \ln T + b_0^{(1)} S^{(0)}_{5/2}(w_1^2) \underline{\underline{b}} : \nabla_{r_1} \underset{\sim}{u} \; . \tag{83}$$

They are

$$\eta_K = - \left(\frac{KT}{2v} \right) b_0^{(1)} \tag{84}$$

$$\eta_v = \left(\frac{KT}{v} \right) \left(\frac{2\pi\sigma^3}{15v} \right) g_0^{(2)}(\sigma) \, b_0^{(1)} \tag{85}$$

$$\varphi_K = \varphi_v \sim b_1^{(2)} \equiv 0 \tag{86}$$

$$\mathcal{K}_K = \frac{5}{2}\left(\frac{m}{T v}\right)\left(\frac{KT}{m}\right)^2\left(\frac{m}{2KT}\right)^{1/2} a_1 \tag{87}$$

$$\mathcal{K}_v = \frac{5}{2}\left(\frac{m g_0^{(2)}(\sigma)}{T v}\right)\left(\frac{KT}{m}\right)^2\left(\frac{m}{2KT}\right)^{1/2}\left(\frac{2\pi\sigma^3}{5v}\right) a_1 \tag{88}$$

We may immediately write the transport coefficients from the modified Fokker-Planck equation which we have solved in Section 3. These are

$$\eta_K = \frac{5}{2} KT \frac{\left[1/g_0^{(2)}(\sigma)\right] + \frac{4\pi\sigma^3}{15v}}{\frac{20}{3}\Omega^{(2,2)} + \left[5\zeta_s v/m g_0^{(2)}(\sigma)\right]} \tag{89}$$

$$\eta_v = \frac{5}{2} KT \frac{\left[1/g_0^{(2)}(\sigma)\right] + \frac{4\pi\sigma^3}{15v}}{\frac{20}{3}\Omega^{(2,2)} + \left[5\zeta_s v/m g_0^{(2)}(\sigma)\right]}\left(\frac{4\pi\sigma^3}{15v}\right) g_0^{(2)}(\sigma), \tag{90}$$

$$\kappa_K = \frac{75}{8}\,\frac{K^2 T}{m}\,\frac{\left[1/g_0^{(2)}(\sigma)\right] + \frac{2\pi\sigma^3}{5v}}{16\,\Omega^{(2,2)} + \left[45\,\zeta_s v/4m\,g_0^{(2)}(\sigma)\right]} \tag{91}$$

$$\kappa_v = \frac{75}{8}\,\frac{K^2 T}{m}\,\frac{\left[1/g_0^{(2)}(\sigma)\right] + \frac{2\pi\sigma^3}{5}}{16\,\Omega^{(2,2)} + \left[45\,\zeta_s v/4m\,g_0^{(2)}(\sigma)\right]}\left(\frac{2\pi\sigma^3}{5v}\right) g_0^{(2)}(\sigma) \tag{92}$$

5. Discussion

The relation of the Rice-Allnatt theory[9,10] to other theories of dense fluids may be studied on the basis of a comparison of the expressions given by these theories for the transport coefficients. Since for all the theories the transport coefficients may be expressed in the form of Eqs. (84) to (88), it is sufficient to compare only the coefficients a_1, $b_o^{(1)}$, $b_m^{(2)}$. There are displayed in Table 1 for (1) the dense fluid hard-sphere fluid,[32] (2) the Rice-Allnatt theory,[9,10] (3) the modified Rice-Allnatt theory of the present paper, and finally, (4) the pure Fokker-Planck theory of Kirkwood.[5] It should be noted that the last mentioned coefficients are obtained when the inhomogeneities $\underline{K}$ and $\underline{\underline{L}}$ are derived entirely from the streaming term Eq. (37).

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32. C. F. Curtiss, "Kinetic Theory of Gases", OOR-3 (January 1953).

Table 1

Comparison of the Coefficients a_1, $b_o^{(1)}$, $b_m^{(2)}$ Appearing in the Perturbation ϕ_1 for Four Different Equations

	a_1	$-b_o^{(1)}$	$b_m^{(2)}$ (all m)
(1) Chapman-Enskog	$\frac{15}{16\Omega^{(2,2)}}\left(\frac{2KT}{m}\right)^{1/2}\left(\frac{v}{g_0^{(2)}(\sigma)}+\frac{2\pi\sigma^3}{5}\right)$	$\frac{5}{4\Omega^{(2,2)}}\left(\frac{v}{g_0^{(2)}(\sigma)}+\frac{4\pi\sigma^3}{15}\right)$	0
(2) Rice-Allnatt	$\frac{15}{4}\left(\frac{2KT}{m}\right)^{1/2}\frac{[v/g_0^{(2)}(\sigma)+2\pi\sigma^3/5]}{[4\Omega^{(2,2)}+[45\zeta_s v/4mg_0^{(2)}(\sigma)]]}$	$5\frac{[v/g_0^{(2)}(\sigma)+4\pi\sigma^3/15]}{[4\Omega^{(2,2)}+[5\zeta_s v/mg_0^{(2)}(\sigma)]]}$	0
(3) Modified Rice-Allnatt	$\frac{15}{4}\left(\frac{2KT}{m}\right)^{1/2}\frac{[v/g_0^{(2)}(\sigma)+\frac{2\pi\sigma^3}{5}]}{[16\Omega^{(2,2)}+[45\zeta_s v/4mg_0^{(2)}(\sigma)]]}$	$5\frac{[v/g_0^{(2)}(\sigma)+4\pi\sigma^3/15]}{[\frac{20}{3}\Omega^{(2,2)}+[5\zeta_s v/mg_0^{(2)}(\sigma)]]}$	0
(4) Fokker-Planck	$\frac{15}{4}\left(\frac{2KT}{m}\right)^{1/2}\frac{v/g_0^{(2)}(\sigma)}{[16\Omega^{(2,2)}+[45\zeta_s v/4mg_0^{(2)}(\sigma)]}$	$5\frac{v/g_0^{(2)}(\sigma)}{[\frac{20}{3}\Omega^{(2,2)}+[5\zeta_s v/mg_0^{(2)}(\sigma)]]}$	0

From the introductory discussion of the Rice-Allnatt equation, it is clear that the coefficients (2) should be of greatest generality, and this is evident from Table 1. It should be noted also that the same structure is exhibited by the coefficients from the modified theory (3), though with some differences in the numerical coefficients which are mentioned again below. The coefficients (1) for the dense hard sphere fluid differ from those of (2) by the omission of the soft friction term in the denominator, while those for the pure Fokker-Planck equation (4) differ from (2) in that the excluded volume term in σ^3 is not present in the numerator.

The appearance of differences in the numerical factors upon comparison of the Rice-Allnatt coefficients and those of the present paper require comment. It was argued in Section 2 of this chapter that the Boltzmann collision integral for a dilute homogeneous gas (i.e., no J_2 term) is equivalent to a Fokker-Planck operator, and this concept was extended to the formally identical term in the Rice-Allnatt equation. It must be pointed out, however, that this equivalence is only exact if the friction coefficient possesses the momentum dependence implicit in the Boltzmann term. This momentum dependence has been thoroughly investigated by O'Toole and Dahler,[27] but the functions they obtain are so complicated that no attempt has been made to incorporate them here. The effect of this momentum dependence, had it been incorporated in our calculation, would have been to alter the weighting of different momentum ranges in obtaining the solutions to the equations, so that different numerical factors would appear multiplying $\Omega^{(2,2)}$ in the solutions for the heat flow and shear parts of the equation. We suggest, but without proof, that this is the reason for the observed differences.

The coefficients $a_n (n > 1)$, $b_n^{(1)} (n > 1)$, $b_n^{(2)} (n > 1)$ (cf. Eqs. (67)—(69)) in the solution of the Chapman-Enskog equation and the Rice-Allnatt equation do not vanish, as ours do, because the functions of $\underline{W}_1$ used in the series expansions of $\underline{A}_1$ and $\underline{\underline{B}}_1$ are not eigenfunctions of the Boltzmann collision integral. However, they are usually assumed to be small. Insofar as the equivalence of our modification of the Rice-Allnatt equation to the original equation is established by the close similarity of the expressions for the transport coefficients, the fact that we find that these coefficients vanish is a strong indication that they are indeed small for the original equation.

We conclude, then, that a Fokker-Planck operator can describe, not only soft rapidly fluctuating forces, but certain types of hard core binary collisions; namely, those satisfying Conditions (b) and (c), and Eq. (5), of Section 2 of this chapter. The omission of the excluded volume terms from (4) shows that the Fokker-Planck operator cannot describe those collisions influenced by the inhomogeneities in density represented by J_2. In other words the Fokker-Planck operator can describe binary collisions in which a large fraction have a grazing character, but cannot describe the predominantly head-on collisions which occur when a system is so dense that grazing collisions are inhibited. Thus the role of hard core collisions in the theory of liquids is to emphasize the importance of collisions resulting in large angle deflections, and this is accomplished by taking account of the fact that the presence of hard cores reduces the available volume.

CHAPTER II

SMALL STEP DIFFUSION MODEL

1. Introduction

The major concern of the statistical theory of transport phenomena in dense fluids is the accurate calculation of the macroscopic fluxes of energy and momentum from the purely microscopic properties of the molecular system. Dilute systems, such as rare gases, have been successfully treated using the Boltzmann equation of transport.[22] This equation can be solved by the methods used in the previous chapter. The properties of the Boltzmann equation are well understood,[33] and its derivation has been carried through using statistical considerations.[1,21] The Boltzmann equation correctly represents the molecular dynamics only when the density is sufficiently low that individual molecules spend a large part of the time moving about freely; that is, when molecules spend a very small part of the time interacting with other molecules. When this is true, the number of three body interactions is infinitesimally small compared to the number of two body interactions, and the transport properties of the gas may be accounted for simply on the basis of binary interactions.

In sharp contrast with the dilute gas, the dense fluid

33. H. Grad, Comm. Pure Appl. Math. 2, 331 (1949).

consists of molecules which are in continuous interaction with their neighbors, and the simplicity of transport by binary collisional transfer of momentum and energy is completely lost. To account for the transport phenomena in these fluids a method which is radically different from that used to understand dilute systems must be adopted.

One very successful method for predicting the transport coefficients has already been mentioned. Starting from the Liouville equation, Kirkwood derived a set of generalized Fokker-Planck equations[5] to describe the evolution in time of the reduced distribution functions. In the course of his analysis he obtained an expression relating the friction coefficient to an integral over the autocorrelation function of the force acting on a single particle. The entire analysis was guided by ideas from the stochastic theory of Brownian motion.[34,35,36] Irving and Kirkwood then derived statistical formulae for the transport coefficients.[31] These formulae were used in conjunction with the moments of the Fokker-Planck equations for the computation of the shear viscosity, and the thermal conductivity of liquid argon. In order to perform the computations accurate pair correlation functions are needed. There have been a few attempts to obtain these functions by neutron or x-ray scattering experiments, but the accuracy

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34. G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. 36, 823 (1930).

35. S. Chandrasekhar, Revs. Mod. Phys. 15, 1 (1943).

36. M. C. Wang and G. E. Uhlenbeck, Revs. Mod. Phys. 17, 323 (1945).

of this work leaves much to be desired. The extant theories are very approximate. When the pair correlation functions obtained from theory and experiment are used to calculate the pressure or heat of vaporization of argon liquid it is found that there is very poor agreement with experiment. In fact these functions give such poor pressures that one is tempted to pay no attention to them at all. Since the transport coefficients can be computed only if these functions are known, one is hard put to test any theory of transport in the dense fluid. Kirkwood and co-workers[37] attempted to improve the pair correlation functions by introducing parameters into them which were subsequently adjusted to give the correct pressure and of heat vaporization. The thermal conductivities and shear viscosities computed by this method were in error by roughly a factor of two.

Kirkwood's equation was then criticized for neglecting the strongly repulsive interaction which takes place when two atoms come very close to one another. This led Rice and Allnatt[9,10] to introduce their model for the important dynamical events in a dense fluid. They argued on the basis of an idealized intermolecular potential. To represent the highly repulsive interactions between the particles they chose a hard core potential and to represent the soft interactions they chose a superposed Lennard-Jones potential. Using Kirkwood's time smoothing techniques, a set of integro-differential equations

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37. R. W. Zwanzig, J. G. Kirkwood, I. Oppenheim, and B. J. Adler, J. Chem. Phys. 22, 783 (1954).

were derived which we shall call "modified Fokker-Planck" equations or Rice-Allnatt equations. These equations describe the motion of a particle on the basis of two widely separated time scales. A particle is imagined to undergo a hard core interaction of zero duration with a neighboring particle, and then to suffer small momentum changes and thereby perform a sort of Brownian motion in the fluctuating force field of its neighbors. Thus the Rice-Allnatt equation consists of two parts; one corresponding to the hard core encounter--an Enskog term, and one corresponding to the Brownian motion--a Fokker-Planck term. These equations, as has been said before, are quite successful in accounting for the transport coefficients of argon, krypton, and xenon.

The Rice-Allnatt equation has again been modified, with some success, as has been thoroughly explained in the preceeding chapter. On the basis of this work the failure of Kirkwood's original equation is fairly well understood.

In all this work, many approximations have been made. Although these approximations have recently been put on a firmer basis by the computer calculations of Rahman,[28] as we shall see later, it is indeed interesting to explore another model first proposed by Rice and Kirkwood;[38] that is, the small step diffusion model. This model will be considerably amplified and some of the more tenous, and in fact poor, approximations will be eliminated.

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38. S. A. Rice, and J. G. Kirkwood, J. Chem. Phys. 31, 901 (1959).

Starting from the exact statistical mechanical equations, Rice and Kirkwood assumed that: (a) the gradient of the pair interaction potential between molecules at time t + s can be expanded in a Taylor series about the gradient at time t, and terms higher than the second may be neglected, (b) the distribution in pair space may be approximated as the product of the local equilibrium pair correlation function in coordinate space and the zeroth order distribution function in momentum space, and (c) the diffusion tensor in pair-space may be approximated as the direct sum of the diffusion tensors in singlet space.

We shall eliminate assumption (c), which is a very poor assumption for dense systems indeed. It should be added here that in (c) a tacit assumption is made that the doublet diffusion coefficient exists, an assumption that must also be made here. This need not be true. This theory shall be used in conjunction with the modified Lennard-Jones potential. Furthermore, the hard-core friction coefficient shall be obtained by an entirely new method. The result is in entire agreement with the Enskog equation, and is quite easily obtained. It does not suffer from the weaknesses of previous derivations which have invariably assumed either (1) hard core collisions are described by a Langevin equation,[39,40] (2) by a

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39. J. T. O'Toole and J. S. Dahler, J. Chem. Phys. 33, 1496 (1961).

40. F. C. Collins and H. Raffel, J. Chem. Phys. 23, 1454 (1955).

Fokker-Planck equation,[41] or (3) the momentum correlation function is exponential.[42]

The treatment of the dense fluid presented herein has a few advantages over the more exact treatments discussed. It relates the coefficient of shear viscosity and thermal conductivity to the diffusion coefficient and other measurable thermodynamic quantities, and thereby circumvents the source of greatest error in any comparison between theory and experiment--the pair correlation function.

2. The Coefficient of Self-Diffusion

We begin by using assumption (a) and (b) to determine the self-diffusion coefficient in a dense fluid whose molecules interact through a modified Lennard-Jones potential, defined as follows:

$$\begin{aligned} V(R_{12}) &= \infty & R_{12} < \sigma \\ V(R_{12}) &= 4\varepsilon\left[\left(\frac{\sigma}{R_{12}}\right)^{12} - \left(\frac{\sigma}{R_{12}}\right)^{6}\right]; & R_{12} > \sigma \end{aligned} \tag{93}$$

The proceedure adopted here is to consider a two component fluid containing N_1 molecules of species 1 and N_2 molecules of species 2, interacting with potentials of intermolecular force V_{11}, V_{12} and V_{22}. Molecules of species 2 are

41. E. Helfand, Phys. of Fluids 4, 681 (1961).

42. H. C. Longuet-Higgins and J. A. Pople, J. Chem. Phys. 25, 884 (1956).

considered identical to the molecules of species 1 in all physical properties except that they are isotopically tagged. In this case V_{11}, V_{12}, and V_{22} are equal, and are represented by Eq. (93).

The dynamical behavior of this system is completely contained in the N-particle distribution function $f^{(N)}(\underline{R}^{(N)}, \underline{P}^{(N)}, t)$, which represents the probability density of finding the system point at $\underline{R}^{(N)}$, $\underline{P}^{(N)}$ in the complete 6N-dimensional phase space of the system (molecules have no internal degrees of freedom). Here $\underline{R}^{(N)}$, $\underline{P}^{(N)}$ represent the N position vectors and N momentum vectors of the N particles in the system. The evolution in time of the N-particle distribution function is given by the Liouville equation.

Kirkwood,[5] showed that any observable quantity may be identified with the ensemble average of the time average of the corresponding microscopic quantity. This statement becomes obvious when it is realized that the measurement process of a time dependent quantity involves the following steps: (1) a system is chosen from an ensemble of identical systems, (2) the time dependent quantity is then observed over a small interval of time over which it is averaged, (3) this procedure is repeated on all the members of the ensemble, and (4) the quantity is averaged over all these measurements.

Kirkwood further showed that the time average and the ensemble average of a dynamical variable can be commuted; that is, that the order in which these averages are performed does not matter. The proof of this statement rests on the fact that $f^{(N)}$ satisfies the Liouville equation. Time and ensemble averages using lower order distribution functions need not commute, and in general do not commute, because these reduced distribution functions do not satisfy Liouville equations, but rather Boltzmann-like equations in their sub-phase-space.

The statements just made may be summarized in the following manner. If $\alpha\,(\underline{R}^{(N)}, \underline{P}^{(N)}, t)$ is a dynamical variable, then the corresponding observable is

$$\langle \alpha(\underline{R}^{(N)}, \underline{P}^{(N)}, t)\rangle = \int\cdots\int d\underline{R}^{(N)} d\underline{P}^{(N)} f^{(N)}(\underline{R}^{(N)}, \underline{P}^{(N)}; t) \frac{1}{\tau}\int_0^{\tau} ds\, \alpha(\underline{R}^{(N)}, \underline{P}^{(N)}; t+s)$$

$$= \int\cdots\int d\underline{R}^{(N)} d\underline{P}^{(N)} \alpha(\underline{R}^{(N)}, \underline{P}^{(N)}; t) \frac{1}{\tau}\int_0^{\tau} ds\, f^{(N)}(\underline{R}^{(N)}, \underline{P}^{(N)}; t+s) \tag{94}$$

where τ is the interval over which α is observed. τ must be chosen such that it is longer than the period of fluctuations in the instrumental recording system. Time smoothing is used as a formal procedure to obtain Markovian kinetic equations from much more complicated non-Markovian kinetic equations. The procedure consists in averaging the distribution functions over an interval of time chosen sufficiently long that memory of some initial state is wiped out. This procedure eliminates transient effects from the kinetic equation, and necessarily wipes out any possibility for a return of the system to its initial state. Thus, irreversibility is introduced into the kinetic equations. Nothing has to be said about the instrumental times. Time smoothing is a formal method whereby information is sacrificed to simplicity. The equations obtained using this procedure can only be used for the computation of transport coefficients in steady state systems, and not for a description of the approach to equilibrium for this requires the detailed knowledge of the memory of the initial state which has been sacrificed. We mention here the instrumental view of time smoothing as it was Kirkwood's view when he first developed the formal procedure, and it is much more concrete.

Using this prescription for finding averages, the number density of particles of species α at the field point $\underset{\sim}{r}_1$, at time t is

$$\rho_\alpha(\underset{\sim}{r}_1) = \left\langle \sum_{i=1}^{N_\alpha} \delta(\underset{\sim}{R}_{\alpha i} - \underset{\sim}{r}_1);\ \bar{f}^{(N)} \right\rangle \tag{95}$$

where $\delta(\underset{\sim}{R}_{\alpha i} - \underset{\sim}{r}_1)$ is a Dirac delta function and

$$\bar{f}^{(N)}(\underset{\sim}{R}^{(N)}, \underset{\sim}{P}^{(N)}; t) = \frac{1}{\tau}\int_0^{\tau} ds\, f^{(N)}(\underset{\sim}{R}^{(N)}, \underset{\sim}{P}^{(N)}; t+s) \tag{96}$$

is the time coarse grained N-particle distribution function at time t, for an ensemble of identical systems and obeys the Liouville equation

$$\frac{\partial \bar{f}^{(N)}}{\partial t} + \sum_{\beta=1}^{2}\sum_{j=1}^{N_\beta}\left\{\frac{\underset{\sim}{P}_{\beta j}}{m_\beta}\cdot\nabla_{R_{\beta j}} + \underset{\sim}{F}_{\beta j}\cdot\nabla_{P_{\beta j}}\right\}\bar{f}^{(N)} = 0 \tag{97}$$

It is now assumed that the molecules in our two component fluid interact with central forces only, the intermolecular potential is a sum of pair potentials and external fields of force are absent. Thus

$$V = \frac{1}{2}\sum_{\beta=1}^{2}\sum_{\alpha=1}^{2}\sum_{j=1}^{N_\beta}\sum_{i=1}^{N_\alpha} V_{\alpha\beta}(R_{\alpha i,\beta j}) \tag{98}$$

where $R_{\alpha i,\beta j} = |\underset{\sim}{R}_{\beta j} - \underset{\sim}{R}_{\alpha i}|$.

The force exerted by βj on αi is

$$\underset{\sim}{F}_{\alpha i}^{\beta j} = \nabla_{R_{\beta j},\alpha i} V_{\alpha\beta}(R_{\alpha i,\beta j}) \tag{99}$$

and the total force acting on particle αi, due to the $N_\alpha - 1$ other α particles, and the N_β, β particles is

$$\underset{\sim}{F}_{\alpha i} = \sum_{\substack{\beta=1 \\ \beta j \neq \alpha i}}^{2}\sum_{j=1}^{N_\beta} \underset{\sim}{F}_{\alpha i}^{\beta j}. \tag{100}$$

The mean force $\overline{\underset{\sim}{F}}_{\alpha}^{(1)}(r_1)$ acting on a molecule of species α located at the field point $\underline{r}_1$ is

$$\rho_\alpha(r_1)\,\overline{\underset{\sim}{F}}_{\alpha}^{(1)}(r_1) = \left\langle \sum_{i=1}^{N_\alpha} \underset{\sim}{F}_{\alpha i}\,\delta(\underset{\sim}{R}_{\alpha i} - \underset{\sim}{r}_1);\, \bar{f}^{(N)} \right\rangle. \tag{101}$$

Multiplying Eq. (97) by $\underline{P}_{\alpha j}\delta(\underline{R}_{\alpha j}-\underline{r}_1)$ and integrating over the whole phase space $d\underline{R}^{(N)}, d\underline{P}^{(N)}$ yields, neglecting inertial terms, and terms of the order of the non-equilibrium terms in the kinetic contribution to the stress tensor,

$$KT\nabla_{r_1}\rho_\alpha(r_1)-\rho_\alpha(r_1)\overline{\underline{F}}_\alpha^{(1)}(r_1) = 0 \tag{102}$$

The temperature in the non-equilibrium system is defined by an ensemble average of the kinetic energy per molecule performed over both components in the fluid. It is assumed that the average kinetic energy per particle is the same for particles of different species.

Bearman and Kirkwood[43] argue that the thermodynamics of isothermal systems in external force fields clearly shows that if the gradient of the chemical potential at a point in the system is equal to the external force at that point then the system is in equilibrium. Thus by imposing a suitable external field on our system we may establish a concentration or chemical potential gradient which is the same as that in the diffusing system we are interested in. By putting this external force into the Liouville equation, Eq. (97) and performing the same operations which led us to Eq. (102) it is found that

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43. R. J. Bearman, J. G. Kirkwood, and M. Fixman, Progress in Statistical Mechanics (Academic Press, New York, 1958), Vol. I.

$$KT\nabla_{r_1}\rho_\alpha(r_1) - \rho_\alpha(r_1)\overline{\underline{F}}_\alpha^{(1,0)}(r_1) = \rho_\alpha(r_1)\nabla_{r_1}\mu_\alpha(r_1). \tag{103}$$

Here $\overline{\underline{F}}_\alpha^{(1,0)}(r_1)$ is the average intermolecular force acting on a particle of species α at a field point $\underline{r}_1$ in the fluid, when such a suitably chosen external force is imposed. Subtracting equation (102) from (103) yields

$$\overline{\underline{F}}_\alpha^{(1)}(r_1) - \overline{\underline{F}}_\alpha^{(1,0)}(r_1) = \nabla_{r_1}\mu_\alpha(r_1). \tag{104}$$

Now the phenomenological equations in irreversible thermodynamics provide a linear relationship between the fluxes of matter in isothermal diffusion and the driving forces for diffusion, which are chemical potential gradients divided by the temperature. When the phenomenological equations for isothermal diffusion in a two component system are inverted, a relation is found which gives the chemical potential gradient in terms of the diffusion velocities of the two components at $\underline{r}_1$

$$\nabla_{r_1}\mu_\alpha(r_1) = N_2\zeta_{12}\left[\underline{u}_2(r_1) - \underline{u}_1(r_1)\right]. \tag{105}$$

Here

$$\rho_\alpha(r_1)\underset{\sim}{u}_\alpha(r_1) = \left\langle \sum_{i=1}^{N_\alpha} \delta(\underset{\sim}{R}_{\alpha i} - \underset{\sim}{r}_1)\frac{\underset{\sim}{P}_{\alpha i}}{m_\alpha} ; \bar{f}^{(N)} \right\rangle,$$

and ζ_{12} is the friction coefficient. Thus, combining Eqs. (13) and (12) it is found that

$$\underset{\sim}{\bar{\bar{F}}}_1^{(1)}(r_1) - \underset{\sim}{\bar{\bar{F}}}_{q}^{(1,0)}(r_1) = N_2\zeta_{12}\left[\underset{\sim}{u}_2(r_1) - \underset{\sim}{u}_2(r_1)\right]. \tag{106}$$

Now the equilibrium force on a particle in the absence of an external field is merely due to the intermolecular interaction. In a system, such as the one we are investigating, the potential of intermolecular interaction between unlike particles is the same as that between like particles. In this case, the equilibrium mean force acting on a diffusing particle in the absence of external forces is zero. Then Eq. (106) becomes

$$\underset{\sim}{\bar{\bar{F}}}_1^{(1)^*}(r_1) = N_2\zeta_{12}\left[\underset{\sim}{u}_2(r_1) - \underset{\sim}{u}_1(r_1)\right] \tag{107}$$

Here $\underset{\sim}{\bar{\bar{F}}}_1^{(1)^*}(r_1)$ is the force which must balance the perturbing external force that must be imposed to create the chemical potential gradient, i.e., the chemical potential gradient itself.

The procedure adopted here, therefore, is to calculate the force on particle α which is necessary to create a relative diffusion velocity $\underset{\sim}{u}_2 - \underset{\sim}{u}_1$ at point $\underline{r}_1$, in the fluid. We proceed to evaluate ζ, where $\zeta = \zeta_{12} + \zeta_{21}$, by first commuting the time and ensemble averages of the force given by Eq. (9) utilizing Eq. (2)

$$\left\langle \underline{F}_{\alpha i}\, \delta(\underline{R}_{\alpha i} - \underline{r}_1);\, \bar{f}^{(N)} \right\rangle = \left\langle \underline{\bar{F}}_{\alpha i}\, \delta(\underline{R}_{\alpha i} - \underline{r}_1);\, f^{(N)} \right\rangle, \tag{108}$$

where $\underline{\bar{F}}_{\alpha i} = \frac{1}{\tau}\int_0^{\tau} \underline{F}_{\alpha i}(t+s)\,ds.$

Using Eqs. (101) and (108) to calculate the average force on a particle of species α located at $\underline{r}_1$, yields

$$\rho_\alpha(r_1)\, \underset{\sim}{\bar{F}}{}^{(1)*}_{\alpha i}(r_1) = \left\langle \sum_{\substack{\beta=1 \\ \alpha i \neq \beta j}}^{2} \sum_{j=1}^{N_\beta} \delta(\underline{R}_{\alpha i} - \underline{r}_1)\, \underset{\sim}{\bar{F}}{}^{\beta j}_{\alpha i}(r_1);\, f^{(N)}(t) \right\rangle. \tag{109}$$

Equation (109) may be written in the following way:

$$\rho_\alpha(r_1)\left\langle \underline{F}_\alpha(r_1)\right\rangle = \int\left[\int\cdots\int \frac{1}{\tau}\int_0^{\tau} ds \sum_{\substack{\beta=1 \\ \beta j \neq \alpha 1}}^{2} \sum_{j=1}^{N_\beta} \underline{F}_{\alpha 1}^{\beta j}(t+s)\, f^{(N)}(t) \right. \tag{110}$$

$$\left. \cdot\, \delta(\underline{R}_{\alpha 1} - \underline{r}_1)\, \delta(\underline{R}_{\beta j} - \underline{R}_{\beta j}^{(0)})\, d\underset{\sim}{R}^{(N)} d\underline{P}^{(N)} \right] d\underline{R}_{\beta j}^{(0)}.$$

The averaging procedure has intentionally been divided into two steps. The first integration averages the force on particle $\alpha 1$ at $\underline{r}_1$ due to particle βj at a fixed distance $\underline{r}_1 + \underline{R}_{\beta j}^{(0)}$ from it, in a medium of N_1+N_2-2 particles. The second integration is over coordinates of particle βj, $\underline{R}_{\beta j}^{(0)}$. Actually the second integration is over the relative position of βj with respect to $\alpha 1$. Thus

$$\rho_\alpha(r_1)\langle \underline{F}_\alpha(r_1)\rangle = \int\left[\int \cdots \int \frac{1}{\tau}\int_0^\tau ds \sum_{\substack{\beta=1 \\ \beta j \neq \alpha 1}}^{2} \sum_{j=1}^{N_\beta} \underline{F}_{\alpha 1}^{\beta j}(t+s)\, f^{(N)}(t) \cdot \delta(\underline{R}_{\alpha 1}-\underline{r}_1)\,\delta(\underline{R}_{\beta j}-\underline{R}_{\beta j}^{(0)})\, d\underline{R}^{(N)} d\underline{P}^{(N)}\right] d\underline{R}_{\beta j,\alpha 1}^{(0)} \tag{111}$$

At this point we introduce the modified Lennard-Jones potential defined by Eq. (93). In this case the force may be divided into two components

$$\underline{F}_{\alpha 1}^{\beta j}(t+s) = {}_H\underline{F}_{\alpha 1}^{\beta j}(t+s) + {}_s\underline{F}_{\alpha 1}^{\beta j}(t+s) \tag{112}$$

where the left-handed subscripts H and s represent the first and second regions in Eq. (93) i.e. the hard and soft components of the intermolecular force.

The average in Eq. (111) may likewise be divided into two parts when Eq. (112) is introduced

$$\rho_\alpha(r_1)\langle \underset{\sim}{F}_{\alpha 1}(r_1)\rangle = \rho_\alpha(r_1)\langle {}^H\underset{\sim}{F}_{\alpha 1}(r_1)\rangle + \rho_\alpha(r_1)\langle {}^S\underset{\sim}{F}_{\alpha 1}(r_1)\rangle \tag{113}$$

where $\langle {}^H\underset{\sim}{F}_{\alpha 1}(r_1)\rangle$ and $\langle {}^S\underset{\sim}{F}_{\alpha 1}(r_1)\rangle$ are obviously

$$\rho_\alpha(r_1)\langle {}^c\underset{\sim}{F}_{\alpha 1}(r_1)\rangle = \sum_{\substack{\beta=1 \\ \beta j \neq \alpha 1}}^{2} \sum_{j=1}^{N_\beta} \int \Big[\int \cdots \int \frac{1}{\tau} \int_0^{\tau} ds\, {}^c\underset{\sim}{F}_{\alpha 1}^{\beta j}(t+s) f^{(N)}(t)$$

$$\cdot\, \delta(\underset{\sim}{R}_{\alpha 1} - \underset{\sim}{r}_1)\, \delta(\underset{\sim}{R}_{\beta j} - \underset{\sim}{R}_{\beta j}^{(0)})\, d\underset{\sim}{R}^{(N)} d\underset{\sim}{P}^{(N)} \Big] d\underset{\sim}{R}_{\beta j, \alpha 1}^{(0)} \tag{114}$$

and c = H or s.

The term $\int_0^{\tau} ds\, {}^H\underset{\sim}{F}_{\alpha 1}^{\beta j}(t+s)$ may be evaluated by considering the hard core collision dynamics. This is a very well known calculation, and will merely be outlined here. One proceeds in the same manner as one does in constructing the collisional contribution to the Boltzmann equation. Should molecules $\alpha 1$ and βj fail to suffer a mutual hard core collision during the interval $(t, t+\tau)$ then the momentum increment, and consequently the above integral will be identically zero. In the event that $\alpha 1$ and βj do collide within τ then

$$\int_0^{\tau} ds\, {}^H\underset{\sim}{F}_{\alpha 1}^{\beta j}(t+s) = \Delta \underset{\sim}{P}_{\alpha 1} = 2\mu_{\alpha\beta}\, \underset{\sim}{K}\underset{\sim}{K}\cdot(\underset{\sim}{C}_{\beta j} - \underset{\sim}{C}_{\alpha 1}) \tag{115}$$

where $\mu_{\alpha\beta} = \frac{m_\alpha m_\beta}{m_\alpha + m_\beta}$, $\underline{k}$ is the unit vector directed from $\alpha 1$ to βj at the instant of their closest approach. The situation would of course be terribly complicated if $\alpha 1$ were allowed to undergo hard core interactions with more than one other particle in the interval τ . To eliminate this possibility we choose τ much larger than the duration of hard core collisions ($0+$) but small enough so that multiple encounters are not permitted. We must also require that τ be no greater than the mean transit time between collisions otherwise we would under-count the number of collisions. A collision cylinder is then constructed around particle 1, and the procedure used is identical to the procedure used in the Rice-Allnatt theory. The basic approximation used here is that the particle trajectories are nearly linear so that the collision cylinder may be extended to the full length $(\underset{\sim}{c}_{\beta j} - \underset{\sim}{c}_{\alpha 1})\tau$ and the cross-section for the collision is unaffected by the presence of the soft force. The effect of this approximation is to underestimate the hard core contribution to the diffusion process, because there will be a higher frequency of hard core collisions due to the existence of the attractive soft force. This can readily be shown by the following argument. Choose a coordinate system which is moving with the velocity of particle 1, and place particle 1 at the origin of this system. Observe the motion of particle 2 relative to the origin of this coordinate system. Consider the assymptotic motion of particle 2, that is, the motion of 2 when its separation from 1 is greater than the range of their intermolecular potential. This assymptotic motion may be specified by an impact parameter b. If the two particles interact according to a hard core potential alone, then, if $b > \sigma$, particle 2 will never undergo a momentum change. If, however, the two particles interact according to a hard core and a superposed Lennard-Jones potential defined in Eq. (93), then, if $b > \sigma$, but is smaller than the range of the soft branch, there may be a hard core interaction. Thus there will certainly be a greater frequency of hard core interactions in a fluid which has Eq. (93) has its potential, than in one which has a hard core alone when these two fluids are at equal temperatures and densities. It is therefore obvious that the procedure we use underestimates the hard contribution. This is also the case in the Rice-Allnatt theory which therefore suffers from the same difficulty.

We have the following set of equations after substituting Eq. (115) into Eq. (114):

$$\rho_\alpha(r_1)\langle {}^H\underset{\sim}{F}_{\alpha 1}(r_1)\rangle = \frac{2}{\tau}\sum_{\substack{\beta=1 \\ \beta j \neq \alpha 1}}^{2}\sum_{j=1}^{N_\beta}\int\left[\int\cdots\int \mu_{\alpha\beta}\underset{\sim}{K}\underset{\sim}{K}\cdot(\underset{\sim}{C}_{\beta j}-\underset{\sim}{C}_{\alpha 1})f^{(2)}(\alpha 1,\beta j)\right. \\ \times\, d\underset{\sim}{P}_{\alpha 1}\,d\underset{\sim}{P}_{\beta j}\,d\underset{\sim}{R}^{(0)}_{\beta j,\alpha 1} \tag{116}$$

where $\underset{\sim}{C}_{\beta j}, \underset{\sim}{C}_{\alpha 1}$ are the velocities of particle βj and $\alpha 1$ before collision. When $f^{(2)}(\alpha 1,\beta j)$ is approximated using assumption (b) in the introduction,

$$f^{(2)}(\alpha 1,\beta j) = g_0^{(2)}(R^{(0)}_{\beta j,\alpha 1})\,f^{(1)}(\beta j)\,f^{(1)}(\alpha 1) \tag{117}$$

where $g_0^{(2)}(R_{\beta j,\alpha 1}^{(0)})$ is the equilibrium pair correlation function and $f^{(1)}(i)$ is the singlet distribution function for particle of type i when account is taken of the conditions necessary to have a collision, it is found that

$$\rho_\alpha(r_1)\langle {}^H\underline{F}_{\alpha 1}(r_1)\rangle = 2\sum_{\beta=1}^{N_\beta} N_\beta \mu_{\alpha\beta} \iint \underline{KK}\cdot(\underline{c}_\beta - \underline{c}_\alpha)\, g_0^{(2)}(\sigma_{\alpha\beta}) \cdot f^{(1)}(\alpha) f^{(1)}(\beta)\, b\, db\, d\varepsilon\, d\underline{c}_\alpha\, d\underline{c}_\beta . \qquad (118)$$

Here $\sigma_{\alpha\beta}$ is the distance between the centers of particles of types α and β when these two particles are in contact, and b is the impact parameter defining the hard core collision, and ε is the azimuthal angle specifying the hard core collision.

To proceed further we must perform a rather tedious set of transformations and angular integrations. First it is necessary to specify the singlet distribution functions that we are using. As stated in the introduction to this chapter these will be chosen as the zeroth order momentum functions, i.e., functions which are Maxwellian about the local velocity,

$$f^{(1)}(\beta) = \rho_\beta \left(\frac{m_\beta}{2\pi KT}\right)^{3/2} \exp - \left[\frac{m_\beta}{2KT}(\underline{c}_\beta - \underline{u}_\beta(r_1))^2 \right]. \qquad (119)$$

In order to use this in Eq. (118) it is necessary to remember that particle α is at $\underline{r}_1$ and β is at $\underline{r}_1 + \sigma_{\alpha\beta}\underline{K}$. Thus Eq. (118) becomes

$$\rho_\alpha(\underline{r}_1)\langle {}^H\underline{F}_{\alpha 1}(\underline{r}_1)\rangle = 2\sum_{\beta=1}^{2} N_\beta \mu_{\alpha\beta}\left(\frac{m_\alpha}{2\pi kT}\right)^{3/2}\left(\frac{m_\beta}{2\pi kT}\right)^{3/2}\rho_\alpha\,\rho_\beta\, g_0^{(2)}(\sigma_{\alpha\beta}) \tag{120}$$

$$\cdot\int\cdot\int \underline{K}\underline{K}\cdot(\underline{c}_\beta-\underline{c}_\alpha)\exp -\beta\left[m_\alpha(\underline{c}_\alpha-\underline{u}_\alpha(\underline{r}_1))^2+m_\beta(\underline{c}_\beta-\underline{u}_\beta(\underline{r}_1+\sigma_{\alpha\beta}\underline{K}))^2\right]$$
$$\cdot\, b\,db\,d\varepsilon\,d\underline{c}_\alpha\,d\underline{c}_\beta$$

where $\beta = \dfrac{1}{2kT}$. We must therefore evaluate the integral

$$\underline{I}_\beta = \underset{\underline{K}\cdot(\underline{c}_\beta-\underline{c}_\alpha)>0}{\int\cdot\int} \underline{K}\underline{K}\cdot(\underline{c}_\beta-\underline{c}_\alpha)\exp -\beta\left[m_\alpha(\underline{c}_\alpha-\underline{u}_\alpha(\underline{r}_1))^2+m_\beta(\underline{c}_\beta-\underline{u}_\beta(\underline{r}_1+\sigma_{\alpha\beta}\underline{K}))^2\right] \tag{121}$$
$$\times\, b\,db\,d\varepsilon\,d\underline{c}_\alpha\,d\underline{c}_\beta ,$$

in terms of which ,

$$\rho_\alpha(\underline{r}_1)\langle {}^H\underline{F}_{\alpha 1}(\underline{r}_1)\rangle = 2\sum_{\beta=1}^{2} N_\beta \mu_{\alpha\beta}\rho_\alpha\rho_\beta (m_\alpha m_\beta)^{3/2}(2\pi kT)^{-3/2} g_0^{(2)}(\sigma_{\alpha\beta})\,\underline{I}_\beta . \tag{122}$$

Let

$$\left\{ \begin{aligned} \underset{\sim}{V}_\alpha &= (\underset{\sim}{C}_\alpha - \underset{\sim}{u}_\alpha(r_1)) \\ \underset{\sim}{V}_\beta &= (\underset{\sim}{C}_\beta - \underset{\sim}{u}_\beta(\underset{\sim}{r}_1 + \sigma_{\alpha\beta}\underset{\sim}{k})) \end{aligned} \right\} \tag{123}$$

Here $\underset{\sim}{V}_\alpha$ and $\underset{\sim}{V}_\beta$ are peculiar velocities. We now perform a series of coordinate transformations. Let

$$\left\{ \begin{aligned} M_{\alpha\beta}\underset{\sim}{X} &= m_\alpha \underset{\sim}{V}_\alpha + m_\beta \underset{\sim}{V}_\beta \\ \underset{\sim}{y} &= \underset{\sim}{V}_\beta - \underset{\sim}{V}_\alpha \end{aligned} \right\} \tag{124}$$

Here $M_{\alpha\beta} = m_\alpha + m_\beta$. $\underset{\sim}{V}_\alpha, \underset{\sim}{V}_\beta$ may be found in terms of $\underline{X}$ and $\underline{y}$.

$$\left\{ \begin{aligned} \underset{\sim}{V}_\alpha &= \frac{1}{M_{\alpha\beta}}(M_{\alpha\beta}\underset{\sim}{X} - m_\beta \underset{\sim}{y}) \\ \underset{\sim}{V}_\beta &= \frac{1}{M_{\alpha\beta}}(M_{\alpha\beta}\underset{\sim}{X} + m_\alpha \underset{\sim}{y}) \end{aligned} \right\} \tag{125}$$

From Eq. (125) it is found that

$$m_\alpha V_\alpha^2 + m_\beta V_\beta^2 = M_{\alpha\beta} X^2 + \mu_{\alpha\beta} y^2 \tag{126}$$

$\underline{X}$ and $\underline{y}$ are the center of mass peculiar velocity and the relative peculiar velocity, respectively. We want to transform these to the center of mass and relative velocities. To do this we first see that

$$\left\{\begin{aligned} M_{\alpha\beta}\underset{\sim}{X} &= m_\alpha \underset{\sim}{C}_\alpha + m_\beta \underset{\sim}{C}_\beta - \left[m_\alpha \underset{\sim}{u}_\alpha(\underset{\sim}{r}_1) + m_\beta \underset{\sim}{u}_\beta(\underset{\sim}{r}_1 + \sigma_{\alpha\beta}\underset{\sim}{K}) \right] \\ \underset{\sim}{y} &= \underset{\sim}{C}_\beta - \underset{\sim}{C}_\alpha - \left[\underset{\sim}{u}_\beta(\underset{\sim}{r}_1 + \sigma_{\alpha\beta}\underset{\sim}{K}) - \underset{\sim}{u}_\alpha(\underset{\sim}{r}_1) \right] \end{aligned}\right\} \tag{127}$$

If we now define the center of mass and relative velocities as

$$\left\{\begin{aligned} M_{\alpha\beta}\underset{\sim}{C}_{\alpha\beta} &= m_\alpha \underset{\sim}{C}_\alpha + m_\beta \underset{\sim}{C}_\beta \\ \underset{\sim}{g}_{\beta\alpha} &= \underset{\sim}{C}_\beta - \underset{\sim}{C}_\alpha \end{aligned}\right\}, \tag{128}$$

and the hydrodynamic center of mass and relative velocity as

$$\left\{\begin{aligned} M_{\alpha\beta}\underset{\sim}{U}_{\alpha\beta} &= m_\alpha \underset{\sim}{u}_\alpha(\underset{\sim}{r}_1) + m_\beta \underset{\sim}{u}_\beta(\underset{\sim}{r}_1 + \sigma_{\alpha\beta}\underset{\sim}{K}) \\ \underset{\sim}{u}_{\beta\alpha} &= \underset{\sim}{u}_\beta(\underset{\sim}{r}_1 + \sigma_{\alpha\beta}\underset{\sim}{K}) - \underset{\sim}{u}_\alpha(\underset{\sim}{r}_1) \end{aligned}\right\}, \tag{129}$$

then Eq. (127) becomes

$$\left\{ \begin{array}{l} \underset{\sim}{X} = \underset{\sim}{C}_{\beta\alpha} - \underset{\sim}{U}_{\beta\alpha} \\ \underset{\sim}{y} = \underset{\sim}{g}_{\beta\alpha} - \underset{\sim}{u}_{\beta\alpha}(\underline{r}_1) \end{array} \right\}, \tag{130}$$

and the result is

$$m_\alpha V_\alpha^2 + m_\beta V_\beta^2 = M_{\alpha\beta}(\underset{\sim}{C}_{\beta\alpha} - \underset{\sim}{U}_{\beta\alpha})^2 + \mu_{\alpha\beta}(\underset{\sim}{g}_{\beta\alpha} - \underset{\sim}{u}_{\beta\alpha})^2. \tag{131}$$

Now

$$(\underset{\sim}{g}_{\beta\alpha} - \underset{\sim}{u}_{\beta\alpha})^2 = g_{\beta\alpha}^2 - 2\,\underset{\sim}{u}_{\beta\alpha}(r_1)\cdot\underset{\sim}{g}_{\beta\alpha} + u_{\beta\alpha}^2. \tag{132}$$

An assumption of this theory is that the relative mean velocity is small, and all second and higher order terms in this variable are negligible. Secondly, it is assumed that the gradients of the mean velocities are small enough that terms of order $(\underset{\sim}{R}\cdot\nabla_R)\underset{\sim}{u}(R)$ are negligible when $\underline{R}$ is of the order of interatomic separations. In this approximation

$$e^{-\beta(m_\alpha V_\alpha^2 + m_\beta V_\beta^2)} = e^{-\beta M_{\alpha\beta}(\underset{\sim}{C}_{\beta\alpha} - \underset{\sim}{U}_{\beta\alpha})^2}\, e^{-\beta\mu_{\alpha\beta}(g_{\beta\alpha}^2 - 2\underset{\sim}{u}_{\beta\alpha}\cdot\underset{\sim}{g}_{\beta\alpha})} \tag{133}$$

the second exponential on the right-hand side of the equation may be expanded about $\underline{u}_{\beta\alpha} = 0$. This gives

$$e^{-\beta(m_\alpha V_\alpha^2 + m_\beta V_\beta^2)} = e^{-\beta M_{\alpha\beta}(\underline{C}_{\beta\alpha} - \underline{U}_{\beta\alpha})^2} e^{-\beta\mu_{\alpha\beta} g_{\beta\alpha}^2} [1 + 2\beta\mu_{\alpha\beta}\, \underline{u}_{\beta\alpha} \cdot \underline{g}_{\beta\alpha}] . \tag{134}$$

When this is put in I_β and the angular and center of mass integrations are performed, it is found that

$$\underline{I}_\beta = \frac{4}{3}\left(\frac{2\pi KT}{\mu_{\alpha\beta}}\right)^2 \sigma_{\alpha\beta}^2\, \underline{u}_{\beta\alpha}(r_1) \tag{135}$$

Thus when this is substituted into Eq. (122) one obtains the result that

$$\rho_\alpha(r_1) \langle {}^H\underline{F}_\alpha(r_1) \rangle = \frac{8}{3} \sum_{\beta=1}^{2} N_\beta (2\pi\mu_{\alpha\beta}KT)^{1/2} g_0^{(2)}(\sigma_{\alpha\beta})\, \sigma_{\alpha\beta}^2 \rho_\alpha \rho_\beta\, \underline{u}_{\beta\alpha}(r_1) . \tag{136}$$

We must now evaluate the soft force contribution to the mean soft force acting on particle α_1 . The soft force contribution may be written down from Eq. (114)

$$\rho_{\alpha}(r_1)\langle {}^{s}\underline{F}_{\alpha 1}(r_1)\rangle = \sum_{\beta=1}^{2}\sum_{j=1}^{N_\beta}\int\left[\int\cdot\int\frac{1}{\tau}\int_0^{\tau} ds\, \nabla_{R_{\alpha 1,\beta j}} V^{s}_{\alpha\beta}(\underline{R}_{\alpha 1,\beta j}(t+s))\, f^{(N)}(t)\right. \tag{137}$$

$$\left.\cdot\,\delta(\underline{R}_{\alpha 1}-\underline{r}_1)\,\delta(\underline{R}_{\beta j}-\underline{R}^{(0)}_{\beta j})\,d\underline{R}^{(N)}d\underline{P}^{(N)}\right]d\underline{R}^{(0)}_{\beta j,\alpha 1}$$

Noting that all the molecules of the same species make the same contribution to the average force on $\alpha 1$ at $\underline{r}_1$, Eq. (137) may be written

$$\rho_{\alpha}(r_1)\langle {}^{s}\underline{F}_{\alpha 1}(r_1)\rangle = \sum_{\beta=1}^{2} N_\beta\int\left[\int\cdot\cdot\int\frac{1}{\tau}\int_0^{\tau} ds\, \nabla_{R_{\alpha\beta}} V^{s}_{\alpha\beta}(R_{\alpha\beta}(t+s))\, f^{(N)}(t)\right. \tag{138}$$

$$\left.\cdot\,\delta(\underline{R}_{\alpha 1}-\underline{r}_1)\,\delta(\underline{R}_{\beta}-\underline{R}^{(0)}_{\beta})\,d\underline{R}^{(N)}d\underline{P}^{(N)}\right]d\underline{R}^{(0)}_{\beta,\alpha 1}\,.$$

This integral may be evaluated using assumption (a) outlined in the introduction. That is

$$\nabla_{R_{\alpha 1,\beta}} V^{s}_{\alpha 1\beta}(\underline{R}_{\alpha 1,\beta}(t+s)) = \nabla_{R_{\alpha 1,\beta}} V^{s}_{\alpha 1,\beta}(\underline{R}_{\alpha 1,\beta}(t)) \tag{139}$$

$$+\left[\Delta\underline{R}_{\alpha 1,\beta}(s)\cdot\nabla_{R_{\alpha 1,\beta}}\right]V^{s}_{\alpha 1,\beta}(\underline{R}_{\alpha 1,\beta}(t)).$$

It is now convenient to introduce the reduced distribution functions $f^{(n)}$ which are related to the probability density $f^{(N)}$ by the definition

$$f^{(N)}(\underline{R}^{(n)},\underline{P}^{(n)},\underline{R}^{(N-n)},\underline{P}^{(N-n)};t) = f^{(n)}(\underline{R}^{(n)},\underline{P}^{(n)};t)\, f^{(n/N-n)}(\underline{R}^{(N-n)},\underline{P}^{(N-n)};t) \tag{140}$$

where $f^{(n|N-n)}$ is the relative probability density in the subspace $\underline{R}^{(N-n)}, \underline{P}^{(N-n)}$, of finding the coordinates and momentum of N-n particles at $\underline{R}^{(N-n)}$ and $\underline{P}^{(N-n)}$ given that the other n particles have specified coordinates and momenta $\underline{R}^{(n)}$ and $\underline{P}^{(n)}$. In the case that the positions and the momenta of a pair of molecules, one from the species α, and the other from the species β, are specified, it is assumed that the pair distribution function may be approximated as in (b) of the introduction. This assumption was also used in Eq. (134). In a similar manner

$$f^{(2)}(\alpha,\beta) = g_0^{(2)}(\underline{R}_{\beta\alpha})\,\rho_\alpha\rho_\beta\,(m_\alpha m_\beta)^{3/2}(2\pi KT)^{-3} e^{-\beta M_{\alpha\beta}(\underline{C}_{\beta\alpha}-\underline{U}_{\beta\alpha})^2} \cdot e^{-\beta\mu_{\alpha\beta} g_{\beta\alpha}^2}\left[1 + 2\beta\mu_{\alpha\beta}\,\underline{u}_{\beta\alpha}(r_1)\cdot \underline{g}_{\beta\alpha}\right]. \tag{141}$$

Here again

$$\underset{\sim}{u}_{\beta\alpha} = \underset{\sim}{u}_{\beta}(\underset{\sim}{r}_1) - \underset{\sim}{u}_{\alpha}(\underset{\sim}{r}_1) + O(\nabla \underset{\sim}{u}) \tag{142}$$

and the terms of order $\nabla \underset{\sim}{u}$ are dropped. Substitution of Eqs. (140), (141) and (142) into Eq. (138), followed by an integration over angles, and over the center of mass velocity yields

$$\begin{aligned}\rho_{\alpha}(r_1)\langle {}^{S}\underset{\sim}{F}_{\alpha 1}(r_1)\rangle = {} & 2\sum_{\beta=1}^{2} \beta N_{\beta}\mu_{\alpha\beta}^{5/2}\rho_{\alpha}\rho_{\beta}(2\pi KT)^{-3/2} \\ & \times \int\!\!\cdot\!\!\int \frac{1}{\tau}\int_0^{\tau}[\Delta \underset{\sim}{R}_{\alpha\beta}(s)\cdot\nabla_{R_{\beta\alpha 1}}\nabla_{R_{\beta\alpha 1}} V^{S}_{\beta\alpha}(R^{(0)}_{\beta\alpha 1})]\, g_0^{(2)}(R^{(0)}_{\beta\alpha}) \\ & \times e^{-\beta\mu_{\alpha\beta} g^2_{\beta\alpha}}\, \underset{\sim}{g}_{\beta\alpha}\cdot \underset{\sim}{u}_{\beta\alpha}\, f^{(2|N-2)}(\alpha\beta|N-2)\, ds\, d^3 g_{\beta\alpha}\, d\underset{\sim}{R}^{(N-2)} d\underset{\sim}{P}^{(N-2)} d\underset{\sim}{R}^{(0)}_{\beta\alpha 1}\end{aligned} \tag{143}$$

$$\begin{aligned}\rho_{\alpha}(r_1)\langle {}^{S}\underset{\sim}{F}_{\alpha 1}(r_1)\rangle = {} & 2\sum_{\beta} \beta N_{\beta}\mu_{\alpha\beta}^{5/2}(2\pi KT)^{-3/2}\int\!\!\cdot\!\!\int \frac{1}{\tau}\int_0^{\tau} ds\, \rho_{\alpha}\rho_{\beta}\, e^{-\beta\mu_{\alpha\beta} g^2_{\alpha\beta}} \\ & \times \underset{\sim}{u}_{\beta\alpha}\cdot \langle \underset{\sim}{g}_{\beta\alpha}\cdot\Delta \underset{\sim}{R}_{\beta\alpha}(s)\rangle^{\alpha,\beta}\cdot\nabla_{R_{\beta\alpha}}\nabla_{R_{\beta\alpha}} V^{S}_{\beta\alpha}(R_{\beta\alpha}(t))\, d^3 g_{\beta\alpha}\, d\underset{\sim}{R}^{(0)}_{\beta\alpha}\end{aligned} \tag{144}$$

with

$$\langle \underset{\sim}{g}_{\beta\alpha}\;\Delta \underset{\sim}{R}_{\beta\alpha 1}(s)\rangle^{\alpha,\beta} = \int\!\cdot\!\cdot\!\int \underset{\sim}{g}_{\beta\alpha 1}\,\Delta \underset{\sim}{R}_{\beta\alpha 1}(s)\, f^{(2|N-2)}(\alpha\beta|N-2)\, d\underset{\sim}{R}^{(N-2)} d\underset{\sim}{P}^{(N-2)} \tag{145}$$

The argument $\alpha\beta|N-2$ of $f^{(2|N-2)}$ indicates that the subset 2 of molecules contains one α and β molecule. To obtain Eq. (144), the fact that the average soft force acting on a molecule of species α in the absence of perturbing forces is zero is used.

The following identity may now be noted.

$$\frac{d}{ds}\Delta \underset{\sim}{R}_{\beta\alpha}(s) = \underset{\sim}{g}_{\beta\alpha}(s) \tag{146}$$

The variable $\underset{\sim}{g}_{\beta\alpha}$ which appears in Eq. (145) must be $\underset{\sim}{g}_{\beta\alpha}^{(0)}$ because the distribution function from which it came originally was $f^{(N)}(t)$ in Eq. (108). The following approximation is now made,

$$\frac{d}{ds}\Delta \underset{\sim}{R}_{\beta\alpha}(s) = \underset{\sim}{g}_{\beta\alpha}(0). \tag{147}$$

This approximation will be put on firmer ground later. Thus Eq. (144) may be simplified by using Eq. (147)

$$\frac{1}{\tau}\int_0^{\tau}\left\langle \underset{\sim}{g}_{\beta\alpha}(0)\,\Delta \underset{\sim}{R}_{\beta\alpha}(s)\right\rangle^{\alpha,\beta} ds = \frac{1}{\tau}\int_0^{\Delta \underset{\sim}{R}_{\beta\alpha}(\tau)}\left\langle d\,\Delta \underset{\sim}{R}_{\beta\alpha}\,\Delta \underset{\sim}{R}_{\beta\alpha}\right\rangle^{\alpha,\beta} \tag{148}$$

$$= \frac{1}{2\tau}\left\langle \Delta \underset{\sim}{R}_{\beta\alpha}(\tau)\,\Delta \underset{\sim}{R}_{\beta\alpha}(\tau)\right\rangle^{\alpha,\beta}$$

The hypothesis of molecular chaos is now introduced as the assumption that a time τ exists which is sufficiently short that the average change in relative displacement $\Delta \underset{\sim}{R}_{\beta\alpha}(\tau)$ is small (assumption (a) in the introduction) but nevertheless, sufficiently long for $\langle \Delta \underset{\sim}{R}_{\beta\alpha}(\tau) \Delta \underset{\sim}{R}_{\beta\alpha}(\tau) \rangle^{\alpha,\beta}$ to reach the assymptotic form $2 \tau \underset{\approx}{\mathcal{D}}^{(2)}_{\beta\alpha}(\underset{\sim}{R}^{(0)}_{\beta\alpha})$, thus allowing the introduction of the generalized pair diffusion tensor in Eq. (148). This diffusion tensor is a function of the initial relative displacement of particle β with respect to α, i.e., $\underset{\sim}{R}^{(0)}_{\beta\alpha}$. This assumption may now be stated as

$$\frac{1}{\tau} \int_0^{\tau} \langle \underset{\sim}{g}_{\beta\alpha}(0)\, \Delta \underset{\sim}{R}_{\beta\alpha}(s) \rangle^{\alpha,\beta} = \underset{\approx}{\mathcal{D}}^{(2)}_{\beta\alpha} (\underset{\sim}{R}^{(0)}_{\beta\alpha}) . \tag{149}$$

Now, the definition of a diffusion coefficient requires a time scale τ long compared to the correlation time of the relative velocity $\underset{\sim}{g}_{\beta\alpha}$. Equation (147) is therefore not valid throughout the whole interval τ , but is valid for times $0 < t << \tau$ such that the relative velocity is highly correlated with its initial value $\underset{\sim}{g}_{\beta\alpha}(0)$. During this latter interval the molecular trajectories are approximately linear. Equation (146) however is valid throughout the interval τ . Equation (149) is therefore approximate. The true equation for $\underset{\approx}{\mathcal{D}}^{(2)}_{\beta\alpha}(\underset{\sim}{R}^{(0)}_{\beta\alpha})$ should be based on Eq. (147); that is

$$\frac{1}{\tau} \int_0^{\tau} \langle \underset{\sim}{g}_{\beta\alpha}(s)\, \Delta \underset{\sim}{R}_{\beta\alpha}(s) \rangle^{\alpha,\beta} ds = \underset{\approx}{\mathcal{D}}^{(2)}_{\beta\alpha} (\underset{\sim}{R}^{(0)}_{\beta\alpha}) \tag{150}$$

If $$\underset{\sim}{g}_{\beta\alpha}(s) = \underset{\sim}{g}_{\beta\alpha}(0) + \Delta\underset{\sim}{g}_{\beta\alpha}(s) \tag{151}$$

then,

$$\underline{\underline{\mathcal{D}}}^{(2)}_{\beta\alpha}(R^{(0)}_{\beta\alpha}) = \frac{1}{\tau}\int_0^\tau \langle \underset{\sim}{g}_{\beta\alpha}(0)\Delta \underset{\sim}{R}_{\beta\alpha}(s)\rangle^{\alpha,\beta} ds \tag{152}$$

$$+ \frac{1}{\tau}\int_0^\tau \langle \Delta\underset{\sim}{g}_{\beta\alpha}(s)\Delta \underset{\sim}{R}_{\beta\alpha}(s)\rangle^{\alpha,\beta} ds$$

The first integral in Eq. (152) is precisely the approximation that was used in obtaining Eq. (149). If the second integral can be proved small compared to the first, then the approximation for $\underline{\underline{\mathcal{D}}}^{(2)}_{\beta\alpha}(R^{(0)}_{\beta\alpha})$ given by Eq. (149) will be justified. Now,

$$\Delta \underset{\sim}{R}_{\beta\alpha}(s) = \int_0^s \underset{\sim}{g}_{\beta\alpha}(s')\,ds' \tag{153}$$

Therefore, substitution of Eq. (153) into the second integral in Eq. (152) yields

$$\langle \Delta\underset{\sim}{g}_{\beta\alpha}(s)\Delta \underset{\sim}{R}_{\beta\alpha}(s)\rangle^{\alpha,\beta} = \int_0^s \Big[\langle \underset{\sim}{g}_{\beta\alpha}(s)\underset{\sim}{g}_{\beta\alpha}(s')\rangle^{\alpha,\beta} \tag{154}$$

$$- \langle g_{\beta\alpha}(0)\, g_{\beta\alpha}(s')\rangle^{\alpha,\beta}\Big]\,ds'$$

The subscripts α, and β on the brackets denote a fixed ensemble average, that is, an average in which the initial positions and momenta of particles α and β are fixed. Thus while $\langle \underset{\sim}{g}_{\beta\alpha}(0)\, \underset{\sim}{g}_{\beta\alpha}(s') \rangle^{\alpha,\beta}$ can be determined by means of an approximate bivarate probability distribution function for $\underset{\sim}{g}_{\beta\alpha}(0)$ and $\underset{\sim}{g}_{\beta\alpha}(s')$ to be simply $\frac{1}{3} g^{(0)}_{\beta\alpha}\, \underset{=}{U}\, \Psi(s')$ where $\Psi(s')$ is the normalized relative velocity autocorrelation function (we assume that the relative velocity is a stationary random process, and for simplicity restrict our attention to the case where different components of the relative velocity are uncorrelated; the argument can be generalized, but is consistent with the assumption of isotropy) and $\underset{=}{U}$ is the unit tensor. The determination of $\langle \underset{\sim}{g}_{\beta\alpha}(s)\, \underset{\sim}{g}_{\beta\alpha}(s') \rangle^{\alpha,\beta}$ requires a knowledge of the trivariate distribution function for $\underset{\sim}{g}_{\beta\alpha}(s)$, $\underset{\sim}{g}_{\beta\alpha}(0)$, and $\underset{\sim}{g}_{\beta\alpha}(s')$. The result is in general a function of $\Psi(s)$, $\Psi(s')$ and $\Psi(s-s')$ for which Eq. (154) does not vanish. For example, consider the case in which the relative velocity is a gaussian random process. In this case it can be shown that

$$\langle \underset{\sim}{g}_{\beta\alpha}(s)\, \underset{\sim}{g}_{\beta\alpha}(s') \rangle^{\alpha,\beta} = \left\{ \frac{\langle g^2_{\beta\alpha} \rangle}{3} \left[\Psi(s-s') - \Psi(s)\Psi(s') \right] + \frac{1}{3} g^2_{\beta\alpha}(0)\, \Psi(s)\Psi(s') \right\} \underset{=}{U} . \tag{155}$$

Substitution of Eq. (155) into Eq. (154) does not cause Eq. (154) to vanish. However, if we average Eq. (155) over $\underset{\sim}{g}_{\beta\alpha}(0)$ we obtain,

$$\langle\langle g_{\beta\alpha}(s)\, g_{\beta\alpha}(s')\rangle^{\alpha,\beta}\rangle = \frac{\langle g^{2}_{\beta\alpha}(0)\rangle}{3}\,\Psi(s-s')\,\underline{\underline{U}} \quad . \tag{156}$$

Here the second bracket denotes this average over $\underset{\sim}{g}_{\beta\alpha}(0)$. This average is in fact performed in Eq. (143). Substituting these results into Eq. (154) it is found that

$$\langle\langle \Delta \underset{\sim}{g}_{\beta\alpha}(s)\,\Delta \underset{\sim}{R}_{\beta\alpha}(s)\rangle^{\alpha,\beta}\rangle = \frac{\langle g^{2}_{\beta\alpha}\rangle}{3}\,\underline{\underline{U}}\int_0^s[\Psi(s-s')-\Psi(s')]\,ds' \tag{157}$$

Since the relative velocity was assumed to be a stationary random process, Eq. (157) can be shown to be zero.

Thus Eq. (149) is a good approximation, and may be substituted into Eq. (144), yielding

$$\rho_\alpha(r_1)\langle {}^{S}\underline{F}_{\alpha 1}(r_1)\rangle = 2\sum_\beta \beta N_\beta \rho_\alpha \rho_\beta (2\pi K T)^{-3} \tag{158}$$

$$\cdot \iint \underline{u}_{\beta\alpha}\cdot \underset{\approx}{D}^{(2)}_{\beta\alpha}(R^{(0)}_{\beta\alpha})\cdot \nabla_{R_{\beta\alpha}}\nabla_{R_{\beta\alpha}} V^{S}(R^{(0)}_{\beta\alpha})\, g^{(2)}_{0}(R_{\beta\alpha})\, e^{-\beta\mu_{\alpha\beta} g^{2}_{\alpha\beta}}\, d\underline{R}^{(0)}_{\beta\alpha}\, d^{3}g_{\beta\alpha}$$

The dependence of $\underline{\underline{\mathcal{D}}}^{(2)}_{\beta\alpha}(R^{(0)}_{\beta\alpha})$ on $R^{(0)}_{\beta\alpha}$ is very weak if $\underline{\underline{\mathcal{D}}}^{(2)}_{\beta\alpha}$ varies very little where the rest of the integrand in Eq. (158) is sharply peaked. This must be considered a model assumption. Thus

$$\underline{\underline{\mathcal{D}}}^{(2)}_{\beta\alpha}(R^{(0)}_{\beta\alpha}) \approx \underline{\underline{\mathcal{D}}}^{(2)}_{\beta\alpha} \tag{159}$$

whereupon Eq. (68) after integrating over $\underline{g}_{\beta\alpha}$ becomes

$$\rho_\alpha(r_1)\langle {}^S\underline{F}_{\alpha 1}(r_1)\rangle = \frac{2}{3}\sum_{\beta=1}^{2} \beta N_\beta \mu_{\alpha\beta}\rho_\alpha\rho_\beta \underline{\underline{\mathcal{D}}}^{(2)}_{\beta\alpha}\cdot \underline{u}_{\beta\alpha}\int \nabla_R^2 \overset{S}{V}(R_{\beta\alpha}) g_0^{(2)}(R_{\beta\alpha})\, d^3R_{\beta\alpha} \tag{160}$$

Combining Eqs. (160), (136) and (113), it is found that

$$\rho_\alpha(r_1)\langle \underline{F}_{\alpha 1}(r_1)\rangle = \sum_\beta N_\beta \Big[\frac{8}{3}(2\pi\mu_{\alpha\beta}KT)^{1/2} g_0^{(2)}(\sigma_{\alpha\beta})\rho_\alpha\rho_\beta\sigma_{\alpha\beta}^2$$

$$+ \frac{2}{3}\mu_{\alpha\beta}\beta\rho_\alpha\rho_\beta \underline{\underline{\mathcal{D}}}^{(2)}_{\beta\alpha}\int \nabla^2_{R_{\beta\alpha}} \overset{S}{V}(R_{\beta\alpha}) g_0^{(2)}(R_{\beta\alpha})\, d^3R_{\beta\alpha}\cdot\Big]\underline{u}_{\beta\alpha} \tag{161}$$

which in the tracer limit becomes

$$\langle \underset{\sim}{F}_1(r_1) \rangle = \rho(r_1) N_2 \left[\frac{8}{3} (\pi m K T)^{1/2} g_0^{(2)}(\sigma) \sigma^2 + \frac{m}{6KT} \mathscr{D}^{(2)} \int \nabla^2 V(R) g_0^{(2)}(R) d^3R \right] \cdot \underset{\sim}{u}_{21} \quad (162)$$

This force on particle 1 is due to the perturbation which causes the relative diffusion velocity $\underset{\sim}{u}_{21}(r_1)$ and must be equal to the force discussed in Eq. (107). We thus identify $\langle \underset{\sim}{F}_1(r_1) \rangle$ with $\overline{\underset{\sim}{F}}{}_1^{(1)*}(r_1)$ and therefore find that the singlet diffusion coefficient, which is $\zeta_{12} + \zeta_{21}$

$$\zeta^{(1)} = \frac{8}{3} \rho (\pi m K T)^{1/2} g_0^{(2)}(\sigma) \sigma^2 + \frac{m \mathscr{D}^{(2)}}{6KT} \rho \int \nabla^2 V(R) g_0^{(2)}(R) d^3R \quad (163)$$

or

$$\zeta^{(1)} = \frac{8}{3} \rho (\pi m K T)^{1/2} g_0^{(2)}(\sigma) \sigma^2 + \frac{m \mathscr{D}^{(2)}}{6KT} \langle \nabla^2 V^s \rangle \quad (164)$$

with $\langle \nabla^2 V^s \rangle$ the equilibrium average of $\nabla^2 V^s$, V^s the soft potential. There are a number of interesting consequences of this equation.

In the absence of the soft potential Eq. (164) becomes

$$\zeta_H^{(1)} = \frac{8}{3}\rho(\pi m K T)^{1/2} g_0^{(2)}(\sigma)\sigma^2 \tag{165}$$

which is precisely the hard core friction coefficient first obtained by Enskog from a solution of the Enskog equation. Helfand,[41] O'Toole and Dahler[39] and Longuett-Higgins and Pople,[42] obtained this result by assuming that hard core molecules in a dense fluid are described by the Langevin stochastic equation of motion. The method used here is superior to these methods in that it is based on a much more satisfactory phenomenology.

If the potential contains no hard core, then Eq. (164) becomes

$$\zeta^{(1)} = \frac{m \mathcal{D}^{(2)}}{6KT} \langle \nabla^2 V \rangle \tag{166}$$

which is precisely the Rice-Kirkwood[38] result. Rice and Kirkwood made the assumption that the pair diffusion tensor could be taken as the sum of the singlet diffusion tensors, or in terms of the coefficients themselves, that

$$\mathcal{D}^{(2)} = 2\,\mathcal{D}^{(1)} \tag{167}$$

It is clear that the pair diffusion coefficient cannot have the form indicated at short intermolecular distances since Eq. (167) implies that the molecules move independently of each other. At what intermolecular distance the deviations from Eq. (167) become significant is unknown. It could well be that the approximation made in taking $\underset{\approx}{\mathcal{D}}^{(2)}_{\beta\alpha}(R^{(0)}_{\beta\alpha})$ out of the integral in Eq. (159) is tantamount to Eq. (167). It then appears that Eq. (167) is valid only in a dilute gas. The hypothesis that Eq. (167) holds in the dense fluid is presently being tested by computer experiments. These authors then find that, on insertion of Eq. (167) into Eq. (166)

$$\zeta^{(1)} = \frac{m}{3} \frac{\mathcal{D}^{(1)}}{kT} \langle \nabla^2 V \rangle, \tag{168}$$

or using the well known Einstein relations ,

$$\mathcal{D}^{(2)} = \frac{kT}{\zeta^{(2)}} \tag{169}$$

$$\mathcal{D}^{(1)} = \frac{kT}{\zeta^{(1)}}, \tag{170}$$

the very well known result ,

$$[\zeta^{(1)}]^2 = \frac{m}{3} \langle \nabla^2 V \rangle \tag{171}$$

is obtained.

When this procedure is carried out for Eq. (164) it is found that

$$\zeta^{(1)} = \zeta_H^{(1)} + \frac{m}{3} < \nabla^2 V^S > \cdot \frac{1}{\zeta^{(1)}} . \tag{172}$$

Thus

$$\zeta^{(1)} = \frac{1}{2} \zeta_H^{(1)} + \frac{1}{2} \left[(\zeta_H^{(1)})^{1/2} + \frac{4m}{3} < \nabla^2 V^S > \right]^{1/2} . \tag{173}$$

An interesting feature of Eq. (173) is that it is quite different from what is usually assumed in the Rice-Allnatt theory. There, $\zeta^{(1)} = \zeta_H^{(1)} + \zeta_S^{(1)}$ is a rigorous consequence of the assumptions but it is assumed that $\zeta_S^{(1)}$ is independent of $\zeta_H^{(1)}$. Here we find this to be untrue. We shall comment on this in a later chapter.

Equation (173) may provide us with a method for evaluating the diffusion coefficient of a gas in the high temperature limit, for then Eq. (167) is exact.

There is yet another possibility. In a separate analysis Rice[44] has obtained the relationships

$$\zeta^{(1)} = [36\pi m c^3 \rho]^{-1} [< \nabla^2 V >]^2 \tag{174}$$

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44. S. A. Rice, Mol. Phys. 4, 305 (1961).

with c = velocity of sound. Thus if Eq. (174) is solved for $\langle \nabla^2 V \rangle$ and substituted into Eq. (166) it is found that

$$\zeta^{(2)} = [\pi m^3 c^3 \rho]^{1/2} [\zeta^{(1)}]^{-1/2} . \tag{175}$$

Rice used an acoustic continuum model, in which it was assumed that the density fluctuations were propagated at the velocity of sound in the fluid. This theory has recently been tested, and it was concluded that the acoustic continuum model does not adequately represent the data. The reason for this probably resides in the fact that the propagation of a density fluctuation depends upon the frequency of that fluctuation, and the velocity c is therefore frequency dependent; a fact which is not considered in the model. Perhaps a method for circumventing this difficulty is to choose that c which gives the correct experimental diffusion coefficient, and then to use this in Eq. (175) to predict $\zeta^{(2)}$.

The best alternative is to use the correct Eq. (166) or (164)

$$\zeta^{(1)} \zeta^{(2)} = \frac{m}{6} \langle \nabla^2 V \rangle \tag{166}$$

or

$$\zeta^{(2)} [\zeta^{(1)} - \zeta_H^{(1)}] = \frac{m}{6} \langle \nabla^2 V^S \rangle . \tag{164}$$

Recently the isotope separation factor for liquid argon has been measured.[18,19,20] From this data the quantity $\langle \nabla^2 V \rangle$ may be found. This, together with diffusion measurements, enables us to evaluate $\zeta^{(2)}$. Equation (164) must be treated slightly differently.

Using the definition of $\langle \nabla^2 V \rangle$,

$$\langle \nabla^2 V \rangle = \rho \int \nabla_R^2 V(R) g_0^{(2)}(R)\, d^3R \tag{176}$$

together with the Laplacian of a centrally symmetric potential

$$\nabla^2 V = \frac{2}{R}\frac{\partial V}{\partial R} + \frac{\partial^2 V}{\partial R^2}, \tag{177}$$

or more particularly the modified Lennard-Jones potential, it is found that

$$\langle \nabla^2 V \rangle = \langle \nabla^2 V^H \rangle + \langle \nabla^2 V^S \rangle, \tag{178}$$

$$\langle \nabla^2 V^H \rangle = \rho \int \left[\frac{2}{R}\frac{\partial V^H}{\partial R} + \frac{\partial^2 V^H(R)}{\partial R^2} \right] g_0^{(2)}(R)\, d^3R, \tag{179}$$

$$\frac{\partial V^H}{\partial R} = -\kappa T\,\delta(R-\sigma). \tag{180}$$

When Eq. (180) is substituted into Eq. (179) and the integration is carried out, it is found that

$$\langle \nabla^2 V^H \rangle = 4\pi\rho\kappa T\left[\frac{\partial g_0^{(2)}(R)}{\partial R}\right]_{R=\sigma}\sigma^2 \tag{181}$$

Combining Eqs. (181), (178), and (164), (165), one finds

$$\zeta^{(2)}\left[\zeta^{(1)} - \zeta_H^{(1)}\right] = \frac{m}{6}\langle \nabla^2 V^S \rangle - \frac{1}{4}(\pi m \kappa T)^{1/2}\left[\frac{\partial}{\partial R}\ln g_0^{(2)}(R)\right]_{R=\sigma}\zeta_H^{(1)}$$

(182)

3. The Shear Tensor

In this section we confine our attention to the soft force contribution to the stress tensor, and the subsequent soft force contribution to the shear and bulk viscosities. The soft contribution to the stress tensor may be written in the following form

$$\underset{\approx}{\sigma}_v^s = \frac{1}{2}\sum_{i\neq j}\sum \int\cdots\int \frac{1}{\tau}\int_0^\tau \underset{\sim}{R}_{ij}\nabla_{R_{ij}} V^s(R_{ij})\,\delta(\underset{\sim}{R}_i-\underset{\sim}{R}_2)\,\delta(\underset{\sim}{R}_j-\underset{\sim}{R}_1)$$
$$\cdot f^{(N)}(t+s)\,ds\,d\underset{\sim}{R}^{(N)}d\underset{\sim}{P}^{(N)}\,d\underset{\sim}{R}_{12}$$

which becomes, after introducing the notation used in the previous section:

$$\underset{\approx}{\sigma}_v^s = \frac{N^2}{2\tau}\int_0^\tau\cdots\int ds \left\langle \underset{\sim}{R}_{12}\nabla_{R_{12}} V^s(R_{12}(t+s))\right\rangle^{1,2} f^{(2)}(1,2)\,d\underset{\sim}{R}_{12}\,d\underset{\sim}{P}_1\,d\underset{\sim}{P}_2 \tag{183}$$

with

$$\left\langle \underset{\sim}{R}_{12}\nabla_{R_{12}} V^s(\underset{\sim}{R}_{12}(t+s))\right\rangle^{1,2} = \int\cdots\int \underset{\sim}{R}_{12}\nabla_{R_{12}} V^s(R_{12}(t+s))\, f^{(2/N-2)}(1,2/N-2)$$
$$\cdot\, d\underset{\sim}{R}^{(N-2)}d\underset{\sim}{P}^{(N-2)}. \tag{184}$$

As in the preceding section, Eq. (139), the gradient of the potential energy may be expanded in a Taylor series retaining only the first two terms. This expansion together with the distribution function given by Eq. (134) is substituted into Eq. (183), to give

$$\underset{=}{\sigma}_V^S = \frac{N^2}{2\tau}\int_0^{\tau}\cdots\int\Big[\Big\langle \underline{R}_{12}\nabla_{R_{12}}V^S(R_{12}) + \underline{R}_{12}\Delta\underline{R}_{12}(s)\cdot\nabla_{R_{12}}\nabla_{R_{12}}V^S(R_{12})\Big\rangle^{1,2}$$

$$+ \Big\langle \Delta\underline{R}_{12}(s)\,\nabla_{R_{12}}V^S(R_{12}) + \Delta\underline{R}_{12}(s)\,\Delta\underline{R}_{12}(s)\cdot\nabla_{R_{12}}\nabla_{R_{12}}V^S(R_{12})\Big\rangle^{1,2}\Big] \tag{185}$$

$$\cdot f_0^{(2)}(1,2)\left[1 + 2\beta\mu_{12}\underset{\sim}{g}_{21}\cdot\underline{u}_{21}\right]d\underline{c}_1\,d\underline{c}_2\,d\underline{R}_{12}\,ds$$

where

$$f_0^{(2)}(1,2) = g_0^{(2)}(R_{12})\rho^2\left(\frac{m}{2\pi KT}\right)^3 e^{-\beta M_{12}(\underline{C}_{12}-\underline{U}_{12})^2} e^{-\beta\mu_{12}g_{12}^2} \tag{186}$$

In the preceding section it was stated that $\underline{u}_{21}$ was the difference in mean velocities between molecules of species one and two both at the point $\underline{R}_1$. This was true because terms of order $\nabla\underline{u}$ were neglected in Eq. (142). In the present treatment it is unnecessary to distinguish between the two species, but it is necessary to retain all terms of order $\nabla\underline{u}$. In fact, it is precisely the velocity flow gradient which acts as the force in the phenomenological law for the flux of momentum, i.e., the Newtonian stress tensor. Therefore terms of order $\nabla \underline{u}$ in $\underline{u}_{21}$ are retained.

$$\underline{u}_2(R_2) - \underline{u}_1(R_1) = \underline{u}_2(R_1) - \underline{u}_1(R_1) + \underline{R}_{12} \cdot \nabla \underline{u} \quad . \tag{187}$$

The soft contribution to the hydrostatic pressure may be separated from the soft contribution to the non-equilibrium part of the stress tensor,

$$\begin{aligned} \underline{\underline{\sigma}}_v^S = \underline{\underline{\sigma}}_v^{(0)} + N^2 \rho^2 \beta \mu_{12} \int \frac{1}{\tau} \int_0^\tau \Big[\Big\langle \Delta \underline{R}_{12}(s) \nabla_{R_{12}} V^S(R_{12}) \underline{g}_{21} \cdot \underline{u}_{21} \\ + \underline{R}_{12} \Delta \underline{R}_{12}(s) \cdot \nabla_{R_{12}} \nabla_{R_{12}} V^S(R_{12}) \underline{g}_{21} \cdot \underline{u}_{21} \Big\rangle^{1,2} \Big] f_0^{(1)}(1) f_0^{(1)}(2) \\ \cdot g_0^{(2)}(R_{12})\, ds\, d\underline{C}_1\, d\underline{C}_2\, d\underline{R}_{12} + \int \Theta(\Delta R_{12}^3) \end{aligned} \tag{188}$$

where $\sigma_v^{(0)}$ is the soft force contribution to the hydrostatic pressure. Terms of order (ΔR_{12}^3) will be neglected. As in Eq. (150) after integration over $\underline{C}_1$ and $\underline{C}_2$, we obtain the result

$$\begin{aligned} \underline{\underline{\sigma}}_v^S = \underline{\underline{\sigma}}_v^{(0)} + \frac{m \vartheta^{(2)}}{4kT} \int \int \Big[\underline{R}_{12} \underline{u}_{12} \cdot \nabla_{R_{12}} \nabla_{R_{12}} V^S(R_{12}) \\ + \underline{u}_{12} \nabla_{R_{12}} V^S(R_{12}) \Big] g_0^{(2)}(R_{12})\, d^3R_{12} \;. \end{aligned} \tag{189}$$

A double gradient $\nabla_R \nabla_R \phi(R)$ may be expressed in the following manner

$$\nabla_R \nabla_R \phi(R) = \hat{e}\frac{\partial}{\partial R}\hat{e}\frac{\partial}{\partial R}\phi(R) \tag{190}$$

$$= \hat{e}\frac{\partial}{\partial R}\hat{e}\,\phi'(R)$$

$$\nabla_R \nabla_R \phi(R) = \hat{e}\left(\frac{\partial \hat{e}}{\partial R}\right)\phi'(R) + \hat{e}\hat{e}\,\phi''(R) \tag{191}$$

with $\hat{e} = \frac{\underset{\sim}{R}}{|R|}$, and $R^2 = x^2 + y^2 + z^2 + z^2$, $\underset{\sim}{R} = \underset{\sim}{i}x + \underset{\sim}{j}y + \underset{\sim}{k}z$.

$$\frac{\partial \hat{e}}{\partial R} = \underset{\sim}{i}\frac{\partial}{\partial R}\left(\frac{x}{R}\right) + \underset{\sim}{j}\frac{\partial}{\partial R}\left(\frac{y}{R}\right) + \underset{\sim}{k}\frac{\partial}{\partial R}\left(\frac{z}{R}\right). \tag{192}$$

Now $\frac{\partial}{\partial R}\left(\frac{x}{R}\right) = \frac{1}{R^2}\left(R\frac{\partial x}{\partial R} - x\right) = \frac{1}{R}\frac{\partial x}{\partial R} - \frac{x}{R^2}$,

and $\frac{\partial x}{\partial R} = \frac{R}{x}$, thus $\frac{\partial}{\partial R}\left(\frac{x}{R}\right) = \frac{1}{x} - \frac{x}{R^2}$.

This proceedure when repeated for the other components yields

$$\frac{\partial \hat{e}}{\partial R} = \frac{\underset{\sim}{i}}{x} + \frac{\underset{\sim}{j}}{y} + \frac{\underset{\sim}{k}}{z} - \frac{1}{R}\hat{e} . \tag{193}$$

Substituting Eq. (193) into Eq. (191) yields

$$\nabla_R \nabla_R \phi(R) = \hat{e}\left[\frac{1}{x}\underset{\sim}{i} + \frac{1}{y}\underset{\sim}{j} + \frac{1}{z}\underset{\sim}{k}\right]\phi'(R) - \frac{\hat{e}\hat{e}}{R}\phi'(R) + \hat{e}\hat{e}\phi''(R) \tag{194}$$

Now

$$\hat{e}\left[\frac{1}{x}\underset{\sim}{i} + \frac{1}{y}\underset{\sim}{j} + \frac{1}{z}\underset{\sim}{k}\right] = \frac{1}{R}(\underset{\sim}{i}x + \underset{\sim}{j}y + \underset{\sim}{k}z)\left(\frac{1}{x}\underset{\sim}{i} + \frac{1}{y}\underset{\sim}{j} + \frac{1}{z}\underset{\sim}{k}\right)$$

$$= \frac{1}{R}(\underset{\sim}{i}\underset{\sim}{i} + \underset{\sim}{j}\underset{\sim}{j} + \underset{\sim}{k}\underset{\sim}{k}) + \frac{1}{R}\begin{pmatrix} 0 & x/y & x/z \\ y/x & 0 & y/z \\ z/x & z/y & 0 \end{pmatrix}$$

$$= \frac{1}{R}\underset{=}{U} + \frac{1}{R}\underset{=}{A}$$

Thus,

$$\nabla_R \nabla_R \phi(R) = \frac{1}{R} \underline{\underline{U}}\, \phi'(R) + \frac{1}{R} \underline{\underline{A}}\, \phi'(R) + \hat{e}\hat{e}\left[\phi''(R) - \frac{1}{R}\phi'(R)\right]. \tag{195}$$

This is different from what Rice and Kirkwood found which was,

$$\nabla_R \nabla_R \phi(R) = \frac{1}{R} \underline{\underline{U}}\, \phi'(R) + R\,\hat{e}\left[\phi''(R) - \frac{1}{R}\phi'(R)\right]. \tag{196}$$

They apparently performed the angular integrations in Eq. (189), and found that $\underline{\underline{A}}$ contributes nothing to the integral. They therefore paid no attention to this term. Using Eq. (195)

$$\nabla_{R_{12}} \nabla_{R_{12}} V^S(R_{12}) = \frac{1}{R_{12}} \underline{\underline{U}}\, V^{S'}(R_{12}) + \frac{1}{R_{12}} \underline{\underline{A}}\, V^{S'}(R_{12}) + \hat{e}_{R_{12}}\hat{e}_{R_{12}}\left[V^{S''}(R_{12}) - \frac{1}{R_{12}} V^{S'}(R_{12})\right]. \tag{197}$$

Substituting Eq. (197) into Eq. (189) yields,

$$\underline{\underline{\sigma}}_v^s = \underline{\underline{\sigma}}_v^{(0)} + \frac{m\Theta^{(2)}}{4KT} N^2 \rho^2 \int\!\!\int [\, \underline{R}_{12}\underline{R}_{12} \cdot \underline{\nabla}\,\underline{u} \cdot \Big[\frac{1}{R_{12}} \underline{\underline{U}}\, V^{s'}(R_{12})$$

$$+ \frac{1}{R_{12}} \underline{\underline{A}}\, V^{s'}(R_{12}) + \hat{e}_{R_{12}}\hat{e}_{R_{12}} [\, V^{s''}(R_{12}) - \frac{1}{R_{12}} V^{s'}(R_{12})] \Big] \Big] g_0^{(2)}(R_{12})\, d^3R_{12} \tag{198}$$

$$+ \frac{m\Theta^{(2)}}{4KT} N^2 \rho^2 \int\!\!\int [\, \underline{R}_{12} \cdot \underline{\nabla}\,\underline{u}\; \hat{e}_{R_{12}} V^{s'}(R_{12})]\, g_0^{(2)}(R_{12})\, d^3R_{12} .$$

$$\underline{\underline{\sigma}}_v^s = \underline{\underline{\sigma}}_v^{(0)} + \frac{m\Theta^{(2)}}{4KT} N^2 \rho^2 \int\!\!\int \Big[\underline{R}_{12}\underline{R}_{12} \cdot \underline{\nabla}\,\underline{u} \cdot \Big[\hat{e}_{R_{12}}\hat{e}_{R_{12}} [\, V^{s''}(R_{12}) - \frac{1}{R_{12}} V^{s'}(R_{12})]$$

$$+ 2\underline{\underline{U}} \frac{1}{R_{12}} V^{s'}(R_{12}) + \underline{\underline{A}} \frac{1}{R_{12}} V^{s'}(R_{12}) \Big] g_0^{(2)}(R_{12})\, d^3R_{12} . \tag{199}$$

The classical Newtonian stress tensor is (Eq. (81)),

$$\underline{\underline{\sigma}} = -\left[p + \left(\tfrac{2}{3}\eta - \varphi\right) \nabla \cdot \underline{u} \right] \underline{\underline{U}} + 2\eta \underline{\underline{\varepsilon}}$$

Equation (199) may be transformed into a form similar to Eq. (81) by writing $\underline{R}_{12}$, $\hat{e}_{R_{12}}$, and $\underline{\nabla}\,\underline{u}$ in spherical polar coordinates and integrating over the polar and azimuthal angles. Identification of the coefficients then leads to

$$\eta_v^s = \frac{m\vartheta^{(2)}}{60KT} N^2 \rho^2 \iint R_{12}^2 \left[V^{s''}(R_{12}) + \frac{4}{R_{12}} V^{s'}(R_{12}) \right] g_0^{(2)}(R_{12}) d^3R_{12} \tag{200}$$

It appears that $\underline{\underline{A}}$ contributes nothing to the stress tensor. Thus Rice and Kirkwood's result is correct.

$$\varphi_v^s = \frac{m\vartheta^{(2)}}{36KT} N^2 \rho^2 \iint R_{12}^2 \left[V^{s''}(R_{12}) + \frac{1}{R_{12}} V^{s'}(R_{12}) \right] g_0^{(2)}(R_{12}) d^3R_{12}, \tag{201}$$

For the coefficients of shear and dialational viscosity. It is important to note that in the transition from Eq. (189) to Eq. (198) we have used the fact that for indistinguishable molecules the term $\underline{u}_2(R_1) - \underline{u}_1(R_1)$ vanishes. When the molecules are distinguishable, as in Section 1, this term is not zero.

4. Thermal Conductivity

In this section we confine attention to the soft contribution to the thermal conductivity. The intermolecular force contribution to the heat flux in a dense fluid system was shown by Irving and Kirkwood[31] to have the form

$$\underset{\sim}{q}^{s}_{v} = \sum_{k}\sum_{\neq i} \int \cdots \int \frac{1}{\tau}\int_0^{\tau} \left[\left[V^{s}(R_{12}) \underset{=}{U} - \underline{R}_{12} \nabla_{R_{12}} V^{s}(R_{12}) \right) \right]$$

$$\cdot \left[\left< \frac{\underline{p}_k}{m_k} \delta(\underline{R}_k - \underline{r}_1)\, \delta(\underline{R}_i - \underline{r}_2\,) ; f^{(N)} \right> \right. \tag{202}$$

$$\left. - \underline{u}(r_1,t) \left< \delta(\underline{R}_k - \underline{r}_1) \delta(\underline{R}_i - \underline{r}_2) ; f^{(N)} \right> \right] ds\, d^3R_{12} .$$

To evaluate the heat flux in a manner similar to the reduction of the stress tensor discussed in the last section, Eq. (202) may be written, after symmetrizing with respect to 1 + 2,

$$\underset{\sim}{q}^{s}_{v} = \frac{N(N-1)}{2} \int \cdot \int \frac{1}{\tau} \int_0^{\tau} \left< \left[V^{s}(R_{12}) \underset{=}{U} - \underline{R}_{12} \nabla_{R_{12}} V^{s}(R_{12}) \right] \cdot \frac{(\underline{C} - \underline{U})}{2} \right>^{1,2}$$

$$\times f^{(2)}(1,2)\, d^3y\, d^3X\, d^3R_{12}\, ds \tag{203}$$

where $(\underline{C} - \underline{U})$ is the peculiar velocity of the center of mass of the pair, i.e., the peculiar velocity ar $\underline{r}_1$ when another molecule is present at $\underline{r}_2$. In a non-isothermal single component system with no bulk matter flow, the distribution function in pair space, $f^{(2)}$, may be expanded in powers of the gradient of the temperature. Starting with Eq. (134) for $f^{(2)}$

$$f^{(2)}(1,2) = \rho^2 g_o^{(2)}(R_{12})\, e^{-\frac{1}{2} m\beta g_{12}^2} e^{-2m\beta X^2}\left[1 + \beta m\, \underline{u}_{21}\cdot \underline{g}_{21}\right] \tag{204}$$

and terminating the Taylor series after the term linear in the gradient operator, it is readily found that

$$f^{(2)}(1,2) = f_o^{(2)}(1,2) + \underline{R}_{12}\cdot \nabla_{R_{12}} f_o^{(2)}(1,2)\,, \tag{205}$$

with

$$\underline{R}_{12}\cdot \nabla_{R_{12}} f_o^{(2)}(1,2) = \left(\frac{\partial f_o^{(2)}}{\partial T}\right)_p \underline{R}_{12}\cdot \nabla_{R_{12}} T\,,$$

so that the perturbed distribution function may be written as

$$f^{(2)}(\underline{R}_{12}, g_{12}, T) = f_o^{(2)}(1,2)\left[1 + \frac{\beta}{T}\left(\mu_{12}\, g_{21}^2 - 3KT\right)\underline{R}_{12}\cdot \nabla T + \left(\frac{\partial}{\partial T}\ln\left[\rho^2 g_o^{(2)}(R_{12})\right]\right)\underline{R}_{12}\cdot \nabla T\right] \tag{206}$$

where as before $f_o^{(2)}$ is the local equilibrium value of the pair distribution function. Using the expansion (b) in the introduction, (neglecting terms which vanish in the integration),

$$\frac{1}{\tau}\int_0^{\tau}\left\langle \left[\underline{\underline{U}}V^{s}(R_{12})-\underline{R}_{12}\nabla_{R_{12}}V^{s}(R_{12})\right]\cdot\frac{(\underline{C}+\underline{U})}{2}\right\rangle^{1,2}ds \tag{207}$$

$$=\frac{m\mathcal{D}^{(2)}}{4}\left[\underline{R}_{12}\cdot\nabla_{R_{12}}\nabla_{R_{12}}V^{s}(R_{12})+2\nabla_{R_{12}}V^{s}(R_{12})\right]$$

The right-hand side of Eq. (117) may be rearranged to

$$\frac{m\mathcal{D}^{(2)}}{4}\left[\hat{e}_{R_{12}}\underline{R}_{12}V^{s''}(R_{12})+2\hat{e}_{R_{12}}V^{s'}(R_{12})\right] \tag{208}$$

$$=\frac{m\mathcal{D}^{(2)}}{4}R_{12}\left(\nabla^{2}_{R_{12}}V^{s}(R_{12})\right)\hat{e}_{R_{12}}$$

When Eqs. (206) and (208) are substituted into Eq. (203), the vectors $\underline{R}_{12}$ and $\hat{e}_{R_{12}}$ are expressed in spherical coordinates, and the polar and azimuthal angles are integrated, after which the relative velocity is integrated, the following result is obtained:

$$\underset{\sim}{q}_{v}^{s}=\left[\frac{N^{2}\mathcal{D}^{(2)}}{24}\int\!\!\cdot\!\int R_{12}^{2}\,\nabla^{2}_{R_{12}}V^{s}(R_{12})\left[\frac{\partial}{\partial T}\rho^{2}g_{0}^{(2)}(R_{12})\right]_{P}d^{3}R_{12}\right]\nabla T. \tag{209}$$

The coefficient of the thermal conductivity is related to the heat flux by Fourier's law i.e.,

$$q_v^s = -K_v^s \nabla T . \tag{210}$$

Comparing Eqs. (210) and (209)

$$K_v^s = \frac{N^2\mathcal{D}^{(2)}}{24} \int\!\!\int R_{12}^2 \nabla_{R_{12}}^2 V^s(R_{12}) \left[\frac{\partial}{\partial T} \rho^2 g_0^{(2)}(R_{12})\right]_p d^3R_{12} . \tag{211}$$

If I is defined as

$$I = \frac{N^2\rho^2}{24} \int\!\!\int R_{12}^2 \nabla_{R_{12}}^2 V^s(R_{12}) g_0^{(2)}(R_{12}) \, d^3R_{12} , \tag{212}$$

the Eq. (211) may be written as

$$K_v^s = -\mathcal{D}^{(2)} \left(\frac{\partial I}{\partial T}\right)_p . \tag{213}$$

5. Approximate Representation of the Transport Coefficients

In this section we shall derive much more convenient formulae for the soft force contribution to the shear viscosity and the thermal conductivity.

We note that for the modified Lennard-Jones potential, the equation of state, and the internal energy of the fluid are

$$\frac{P}{\rho KT} = 1 - \frac{2\pi\sigma^3}{3}\rho\, g_0^{(2)}(\sigma) - \frac{\rho}{6KT}\iiint R_{12}\, V^{s\prime}(R_{12})\, g_0^{(2)}(R_{12})\, d^3R_{12} \tag{214}$$

and

$$\frac{E}{NKT} = \frac{3}{2} + \frac{\rho}{2KT}\iiint V^{s}(R_{12})\, g_0^{(2)}(R_{12})\, d^3R_{12} \; . \tag{215}$$

where P is the equilibrium hydrostatic pressure and E is the internal energy. Comparing Eqs. (200), (201) and (213) with Eqs. (214) and (215) it is easily seen that the integrands are very similar in structure. Introducing the definitions:

$$B_6 = 4\varepsilon\rho \iiint \left(\frac{\sigma}{R_{12}}\right)^6 g_0^{(2)}(R_{12})\, d^3R_{12} \, , \tag{216}$$

$$B_{12} = 4\varepsilon\rho \iiint \left(\frac{\sigma}{R_{12}}\right)^{12} g_0^{(2)}(R_{12})\, d^3R_{12} \, . \tag{217}$$

the Eqs. (214) and (215) may be written as

$$\frac{P}{\rho KT} = 1 + \frac{2\pi\sigma^3}{3}\rho g_0^{(2)}(\sigma) + \frac{1}{KT}[2B_{12} - B_6], \tag{218}$$

and

$$E - \frac{3}{2}NKT = L = \frac{1}{2}N(B_{12} - B_6), \tag{219}$$

respectively. L is the heat of vaporization of the fluid. Solving Eqs. (218) and (219) for B_6 and B_{12} yields

$$B_6 = KT\left[\frac{P}{\rho KT} - 1 - \frac{2\pi\sigma^3}{3}\rho g_0^{(2)}(\sigma)\right] - \frac{4L}{N} \tag{220}$$

$$B_{12} = KT\left[\frac{P}{\rho KT} - 1 - \frac{2\pi\sigma^3}{3}\rho g_0^{(2)}(\sigma)\right] - \frac{2L}{N}. \tag{221}$$

From Eqs. (200) and (201) we find that

$$\eta_v^s = \frac{mN^2\mathcal{D}^{(2)}}{10KT}\rho\,[18B_{12} - 3B_6] \tag{222}$$

$$\phi_v^s = \frac{mN^2\mathcal{D}^{(2)}\rho}{KT}\left[4B_{12} - B_6\right], \tag{223}$$

or in terms of the thermodynamic variables

$$\eta_v^s = \frac{mN^2\mathcal{D}^{(2)}\rho}{10KT}\left[15KT\left[\frac{P}{\rho KT} - 1 - \frac{2\pi\sigma^3}{3}\rho g_0^{(2)}(\sigma)\right] - \frac{24L}{N}\right] \tag{224}$$

$$\phi_v^s = \frac{mN^2\mathcal{D}^{(2)}\rho}{KT}\left[3KT\left[\frac{P}{\rho KT} - 1 - \frac{2\pi\sigma^3}{3}\rho g_0^{(2)}(\sigma)\right] - \frac{4L}{N}\right]. \tag{225}$$

From Eqs.(212) and (87) a similar relationship may be obtained for the thermal conductivity

$$I = \frac{N^2\rho}{4}\left[22B_{12} - 5B_6\right] \tag{226}$$

or, in terms of the thermodynamic variables,

$$I = \frac{N^2\rho}{4}\left[17KT\left[\frac{P}{\rho KT} - 1 - \frac{2\pi\sigma^3}{3}\rho g_0^{(2)}(\sigma)\right] - \frac{24L}{N}\right]. \tag{227}$$

Taking the temperature derivative of I and substituting into Eq. (213) yields

$$K_v^s = -\rho \frac{\vartheta^{(2)}}{N}\Bigg[\frac{17}{4}R\Big[\rho(1-\alpha T) + \frac{2\pi\sigma^3}{3}\rho\Big(\Big[\frac{\partial}{\partial T}g_0^{(2)}(\sigma)\Big]_P - 2\alpha g_0^{(2)}(\sigma)T + g_0^{(2)}(\sigma)\Big) + 6\Big(\alpha L + \frac{7}{2}R - C_p^{\ell}\Big)\Bigg], \tag{228}$$

with α the coefficient of thermal expansion and C_p^{ℓ} the heat capacity at constant pressure of the liquid. We now proceed to evaluate these quantities numerically for liquid argon.

4. Numerical Calculations

We have on several occasions remarked that the Rice-Allnatt theory was in good agreement with the observed transport coefficients. How meaningful is this statement? As is well known, the available pair correlation functions of either experimental or theoretical origin are very poor. In this section we examine some of the consequences of the errors in $g_o^{(2)}(R)$ and V (R). Attention is focused on the coefficients of thermal conductance and shear viscosity.

Let us first examine the accuracy with which the radial distribution function and potential reproduce the equilibrium internal energy and pressure of the liquid. It is well known that the calculation of the pressure is inordinately sensitive to the relative positions of the minimum of V(R) and the first maximum of $g_o^{(2)}(R)$,[45,46] and that the internal energy is less sensitive to error than is p. In Table 2 there are displayed the theoretical and experimental[47] values of L (defined by Eq. (215)) for the potential parameters $\varepsilon = 171 \times 10^{-16}$ $\sigma = 3.418 \times 10^{-8}$ cm, and the same radial distribution functions used by Ikenberry and Rice in the theory of thermal conductance. The agreement, while not spectacularly good, is satisfactory. On the other hand, in Table 3 are displayed the calculated pressures. These are seen to be in very poor agreement with observation. The sensitivity of the calculated pressure to a change in well depth, ε , with no change in σ is easily seen by comparison of the third and fourth columns of Table 3. The change in well depth from $\varepsilon/k = 123.8^{o}$K to $\varepsilon/k = 115^{o}$K is within the experimental uncertainty of the potential. Indeed, it is found that no single set of parameters (ε , σ) adequately describes the temperature dependence of the second virial coefficient. At the high temperature end of the experimental data the set ($\varepsilon/k = 123.8^{o}$, $\sigma = 3.418$ A) fits, whereas at the low-temperature end the parameter set ($\varepsilon/k = 115^{o}$, $\sigma = 3.50$ A) is required to effect a fit to the data. This indicates that the Lennard-Jones potential is inadequate over the entire range and a different analytic form

45. M. Klein, Ph.D. Thesis, Department of Physics, University of Maryland, 1962.

46. F. Buff, Ph.D. Thesis, Department of Chemistry, California Institute of Technology, 1949.

47. F. Dunn, Thermodynamic Functions of Gases (Butterworths Scientific Publications, L. + d., London, 1956), Vol. 2.

a more flexible form of the potential is needed. Is the discrepancy between the calculated and observed pressures indicative of gross errors which vitiate the meaningfulness of any calculations of transport coefficients? We believe the answer to this question is no. Consider, for example, an alteration of the potential such as to make the pressure integral correct. This may be done in a variety of ways since all that is needed is a shift of the minimum of the potential relative to the first maximum of $g^{(2)}(R)$. Arbitrarily, we choose to alter V(R) by scaling the potential through introduction of a parameter c,

$$V(R) = 4\varepsilon\left[\left(\frac{\sigma}{cR}\right)^{12} - \left(\frac{\sigma}{cR}\right)^{6}\right] \tag{229}$$

but we do not alter $g_0^{(2)}(R)$. The values of the parameter c are entered in Table 3 from which it is seen that the small shift in potential which is required, of the order of 1%-2% is within the uncertainty in V(R). Although the procedure adopted is arbitrary, we assert that it is a useful technique for improving integrands which involve products of widely varying functions, each of which is subject to uncertainty. It is important to note that the shift required in V(R) is very small. Since the shape of V(R) is not completely correct and the parameters are subject to uncertainties greater than the shift required, we shall use the shifted potential as a test function to examine the numerical stability of the computed transport coefficients.

Table 2

Theoretical and Experimental Internal Energies for Liquid Ar

T^{o}(K)	p(atm)	L(calc) (J)	L(obs)
128	50	-5150	-3345
135.5	100	-5136	-3474
185.5	500	-5074	-3456

We proceed by first noting that the use of the shifted potential in Eq. (210) leads to only small changes in the computed values of L. Consider now the computation of the thermal conductivity. Ikenberry and Rice[14] have shown that κ_{V}^{S} depends on the difference between V(R) and RV'(R). Introduction of the shifted potential then, in effect, leads to the multiplication of κ_{V}^{S} by c, since the difference between V(R) and RV'(R) causes cancellation of the effect of all but one of the powers of c which enter from Eq. (139). The computed thermal conductance is, therefore, essentially unaffected by the shift of the potential required to correct the pressure integral.

Consider now the computation of η_{V}^{S} . Lowry, Rice and Gray[15] have shown that in this case the integrand is of the form $\Psi_2(R) R^3 V'(R) g_0^{(2)}(R)$ and all the functions vary widely as R ranges from σ to ∞ . Moreover, the function Ψ_2(R) is determined from the solution of a differential equation, the input of which requires $g_o^{(2)}(R)$. We may therefore expect η_V^S to be very sensitive to the relative positions of $V(R)$, $g_o^{(2)}(R)$, and $\psi_2(R)$. Detailed calculation shows that the introduction of the scaled potential leads to 25% changes in η_V^S but only 5% changes in the total shear viscosity. For example, at 100 atm and 133.5°K, the raw potential leads to $\eta_V^S = .1898 \times 10^{-3}$ poise whereas the scaled potential leads to $\eta_V^S = .2228 \times 10^{-3}$ poise. Correspondingly, the total computed shear viscosity changes from $\eta_T = .701 \times 10^{-3}$ poise to $\eta_T = .730 \times 10^{-3}$ poise. It should be noted that the shear viscosity is sensitive to σ in three ways: σ^5 and σ^6 appear in the equations, the hard-core contribution is quite important, and the hard-core contribution is sensitive to $g_o^{(2)}(\sigma)$. In all, it appears that the shear viscosity is much more sensitive to the potential and to $g_o^{(2)}(R)$ than is the thermal conductance (compare pressure and internal energy). Within the uncertainties of our knowledge of $V(R)$ and the inadequacy of $g_o^{(2)}(R)$, it still appears that the computed viscosity is only variable by an order 25% within the range of possible variation of ε, σ, and $g_o^{(2)}(\sigma)$. Changes of $g_o^{(2)}(R)$ cannot at present be investigated arithmetically because of the unavailability of suitable theoretical or experimental functions.

We conclude that the agreement between the Rice-Allnatt theory and experiment is meaningful since the possible changes in computed coefficients are bounded in a reasonable domain. This conclusion is supported by the observation that agreement between theory and experiment exists in numerous cases of independent calculation. The likelihood that all such independent calculations are spuriously correct seems small.

Table 3

Theoretical and Experimental Pressures for Liquid Ar

T^{o}(K)	p(obs)	p(calc)[a] (atm)	p(calc)[b]	c
128	50	-306	-190	0.9819
135.5	100	-228	-112	0.9827
185.5	500	+284	+398	0.9887

[a] $/k = 123.8^{o}$K

[b] $/k = 115^{o}$K

For our calculations of the doublet friction coefficient we shall use the values of $\langle \nabla^2 V \rangle$ deduced from isotope separation data, rather than those computed with a theoretical radial distribution function. To compute the shear viscosity and thermal conductivity we must have values for the contact pair correlation function and its temperature derivative. These values are obtained from the Kirkwood integral equation. It is found that the coefficients are not very sensitive to these functions, so that our results are insensitive to the weaknesses of the equilibrium theory. There is, however, one exception to this statement: The doublet friction coefficient calculated from Eq. (182) and tabulated in Table 4 as $\zeta_E^{(2)}$. All calculations are for Ar at 90°K, and 1 atm pressure.

When the singlet friction coefficient $\zeta^{(1)}$ is computed from Eq. (174) it is found to be approximately three times too large, but when it is computed from Eq. (168) it is very close to the observed value $\zeta_{obs}^{(1)}$. Thus instead of using the measured velocity of sound to compute the doublet diffusion coefficient, in Eq. (175) we adopt the follwoing procedure. A value of c which we will call c* is chosen such that Eq. (174) gives the correct singlet friction coefficient. This value of c is then used in Eq. (175) to find $\zeta^{(2)}$. The value of $\zeta^{(2)}$ found in this way is tabulated in Table 4 as $\zeta_A^{(2)}(c^*)$ The value of $\zeta^{(2)}$ found from Eq. (175) using the measured value of c is tabulated in Table 4 as $\zeta_A^{(2)}(c)$, but is not used in the computation of the transport coefficients. Eq. (166) and Eq. (182) are used to compute the doublet friction coefficient, and are tabulated in Table 4 as $\zeta_c^{(2)}$ and $\zeta_E^{(2)}$ respectively. To check the accuracy of the value of $\zeta_E^{(2)}$, the singlet friction coefficient is calculated by Eq. (172) and is tabulated in Table 4 as $\zeta_D^{(1)}$. $\zeta_D^{(1)}$ is about 20% too high. Thus we should not have too much confidence in $\zeta_E^{(2)}$.

The soft components of the shear viscosity and thermal conductivity are then computed. These coefficients are tabulated in Table 5 as η^S_{VA}, η^S_{VC}, η^S_{VE}, K^S_{VA}, K^S_{VC}, K^S_{VE}, respectively. The superscript S denotes "soft component", and the subscripts A, C, and E are used to label the doublet friction coefficient used in the computation. These transport coefficients are then compared with the soft contributions computed by means of the Rice-Allnatt equation and agreement with this more exact theory is found to be excellent.

The justification of the assumptions made here regarding the existence of the pair diffusion tensor and its weak dependence on $\underline{R}_{12}$, must await a more precise theory. Rahman, whose work will be discussed in Chapter IV, is checking the validity of these assumptions by performing a computer experiment. Furthermore the validity of the expansion of the pair potential is being checked. It might be pointed out that for a harmonically bound particle the expansion is exact, because the third and higher order derivatives are identically zero. If $\Delta\underline{R}_{12}(S)$ is small for times of order τ, then the higher powers of $\Delta\underline{R}_{12}$ would annihilate the higher derivatives. This, as has been said, is being investigated by Rahman.

The agreement with the Rice-Allnatt theory is indeed surprising, because the model used is very simple. We believe that the small step diffusion model is a simple intuitive model which incorporates the physical features of a dense fluid.

Table 4

The Singlet and Doublet Diffusion Coefficients

T ^{o}K	P atm	ρ g/cc	c $\frac{cm}{sec}$	c^* $\frac{cm}{sec}$	$\langle \nabla^2 V \rangle_{obs}$ $\frac{ergs}{cm^2} \times 10^{-3}$	$\langle \nabla^2 V^s \rangle$ $\frac{ergs}{cm^2} \times 10^{-3}$
90	1.3	1.374	8.196	11.81	11.25	10.96

Table 4--Continued

$\zeta_{obs}^{(1)}$	$\zeta_H^{(1)}$	$\zeta_A^{(1)}$	$\zeta_B^{(1)}$	$\zeta_O^{(1)}$	$\zeta_A^{(2)}(c)$	$\zeta_A^{(2)}(c^*)$	$\zeta_C^{(2)}$	$\zeta_E^{(2)}$
4.93	0.64	14.8	5.0	5.68	1.61	2.52	2.52	2.84

All ζ are in units of $\frac{gm}{sec} \times 10^{10}$.

Table 5

Shear Viscosity[a] and Thermal Conductivity[b]

Comparison Between Small Step Diffusion Model and Rice-Allnatt Theory

	Rice-Allnatt	R	C	E
η_K	.031			
$\eta_v^{(1)}(\sigma)$	.012			
$\eta_v^{(2)}(\sigma)$	.282			
$\eta_v^{(3)}(\sigma)$	.155			
η_v^S	.926			
		.921	.921	.863
	1.256+			
η_{TOT}	1.121			
		1.401	1.401	1.343
	1.74+			
η_{obs}	2.39			
κ_K	.020			
$\kappa_v^{(1)}(\sigma)$	.017			
$\kappa_v^{(2)}(\sigma)$	.198			
κ_v^S	.822			
		1.26	1.26	1.12
	1.410+			
κ_{TOT}	1.057			
		1.495	1.495	1.355
	1.645+			
κ_{obs}	2.96			

[a]All η are in units of 10^{-3} poise.

[b]All κ are in units of 10^{-4} cal/deg cm sec.

CHAPTER III

THE IDEAL IONIC MELT

1. Introduction

From the experimental evidence accumulated in the past decade it has become apparent that many of the properties of ionic melts are similar to the corresponding properties of dense fluids composed of molecules which interact with a short-range intermolecular potential.[48] This is an interesting observation in view of the marked differences in behavior between dilute solutions of electrolytes and dilute solutions of non-electrolytes.[49,50] It is therefore clear that the role of the long-range Coulomb potential in determining the properties of a dense fluid must be examined carefully.

The Coulomb potential differs from van der Waals type potentials in three respects: (i) The range of the potential

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48. See, for example, Discussions Faraday Soc. 32, 1961.

49. H. S. Haned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions (Reinhold Publishing Corporation, New York, 1959), 3rd ed.

50. J. H. Hildebrand and R. L. Scott, Solubility of Non-Electrolytes (Reinhold Publishing Corporation, New York, 1949).

is infinite (that is,

$$\int \frac{d^3 R}{R}$$

is a divergent integral); (ii) The Coulomb interaction may be either attractive or repulsive dependent only on the signs of the pair of charges; (iii) The Coulomb potential is very much greater in strength than ordinary van der Waals potentials. As a consequence of characteristic (ii) and (iii), it is impossible to have macroscopic deviations from electroneutrality. Moreover, the structural polarization in a fluid of positive and negative charges implied by Conditions (ii) and (iii) is such as to screen the Coulomb potential, decreasing the effective range to the order of molecular dimensions. As a consequence of this polarization and shielding, the divergence catastrophies implied in (i) are avoided.

By the term ideal ionic melt we mean a fluid which consists of spherically symmetric ions, interacting pairwise with a potential consisting of a rigid impenetrable core, a short-range van der Waals potential and the long-range interaction or repulsion characteristic of the Coulomb potential. This fluid contains oppositely charged ions of nearly equal size and with identical electronic properties (except for the sign of the charge. As remarked above the condition of strong local electroneutrality leads to configurations in which a positive ion is on the average surrounded by negative ions and vice versa.[51] Thus the most likely hard-core encounters occur between oppositely charged ions. In the analysis of the properties of the ideal ionic melt we go further and assume that the only role of the Coulomb potential is to determine the local structure of the melt, and thereby to determine the two-body dynamics. We note that hard-core interactions between like charged ions are rendered unlikely by both structural and energetic considerations. In a previous analysis of the ionic melt, Rice[52] has shown by direct calculation that the Coulomb potential does not contribute significantly to the transport properties of the melt. Rice finds that the Coulombic contribution to the friction coefficient for a typical ionic melt is of order 10^{-12} to 10^{-13} g/sec whereas the observed friction coefficients are of order 10^{-10} g/sec; It is therefore concluded that dissipation in these melts is the result of the short range part of the intermolecular potential. Another very simple argument can be given to make this statement plausible. The approximate theory for the friction coefficient given in the last chapter by Eqs. (168) and (175) may be used here. Both of these equations involve the quantity $\langle \nabla^2 V \rangle$. The Coulomb potential satisfies LaPlace's equation; therefore, for the Coulomb potential $\langle \nabla^2 (\frac{1}{R}) \rangle \equiv 0$. In this very simple way we see that the Coulomb potential contributes nothing to the friction coefficient, and thus very little to the

51. F. H. Stillinger, J. G. Kirkwood, and P. J. Wojtowicz, J. Chem. Phys. 32, 1837 (1960).

52. S. A. Rice, Trans. Faraday Soc. 58, 499 (1962).

transport coefficients. We therefore assert as a model assumption that the Coulomb potential plays only the indirect role cited in determining the transport properties of the ideal ionic melt. We see later that this assumption allows us to consider an ideal ionic melt to be a pseudo-two component system.

2. Transport Equation: Singlet Distribution Function

It is convenient to enumerate once again as a set of specific assumptions the conditions which define the ideal ionic melt.

(1) Oppositely charged ions are of nearly equal size and have identical electronic properties (except for the sign of the charge).

(2) Strict local electroneutrality requires that on the average a positive ion is surrounded by negative ions, and vice versa. Thus the most likely hard-core collisions occur between oppositely charged ions.

(3) The probability of a hard-core collision between like ions is reduced by the Coulomb repulsion between them--hence these collisions make a very small contribution to the transport properties of a melt and are neglected in the following analysis.

(4) The total pair potential is the sum of three terms: a rigid-core repulsion, a van der Waals type attraction and repulsion, and a Coulomb attraction or repulsion modulated by the polarization of the surrounding fluid.

(5) The Coulomb potential gives rise to a large cohesive

energy and determines the local structure and thereby the two-body dynamics in the fluid, but does not contribute directly to the transport of momentum or energy.

With the preceding assumptions, we have derived an integro-differential equation using the basic method of the Rice-Allnatt theory of liquids.[9,10] We present the details of this derivation in Appendix. The derivation proceeds by first deducing Rice-Allnatt type equations for a general binary mixture and then specializing these results to the case of the ideal ionic melt. It is Assumption (3) which greatly simplifies the structure of these equations. This condition, in fact, reduces the problem from that of a binary mixture to that of a pseudo two-component fluid. We present here only the results of the derivation for the singlet distribution function. In the following sections we discuss the corresponding doublet equation.

The analysis displayed in the Appendix shows that the singlet distribution function of an ideal ionic melt satisfies an equation identical in structure with that for a pure fluid. There are two singlet equations which are identical except for the identity of the particles to which they refer. For example, for species α, $\bar{f}^{(1)}(\alpha)$ satisfies the equation

$$D_\alpha^{(1)} \bar{f}^{(1)}(\alpha 1) = J_{1\alpha\beta} + J_{2\alpha\beta} + (\zeta_{\alpha\alpha} + \zeta_{\alpha\beta}) A_{\alpha 1}^{(1)} \bar{f}^{(1)}(\alpha 1), \tag{230}$$

with

$$D_{\alpha}^{(1)} = \left(\frac{\partial}{\partial t}\right) + \frac{1}{m_\alpha} \underline{P}_{\alpha 1} \cdot \nabla_{R_{\alpha 1}} + \nabla_{P_{\alpha 1}} \cdot \underline{F}_{\alpha 1}^{*}, \tag{231a}$$

$$A_{\alpha 1}^{(1)} = \nabla_{P_{\alpha 1}} : \left[\frac{1}{m_\alpha} \underline{P}_{\alpha 1} + KT \nabla_{P_{\alpha 1}}\right], \tag{231b}$$

$$\underline{F}_{\alpha 1}^{*} = {}^{(1)}\langle {}^{s}\underline{F}_{\alpha 1} \rangle^{0} + \underline{F}_{\alpha 1}^{+} \tag{231c}$$

$$\begin{aligned} J_{1\alpha\beta} = g_0^{(2)}(\sigma_{\alpha\beta}) \int \cdots \int \Big[& \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\alpha 1} - \Delta \underline{P}_{\alpha 1}; t) \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\beta 1} - \Delta \underline{P}_{\beta 1}; t) \\ & - \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\alpha 1}; t) \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\beta 1}; t) \Big] \cdot \left| \frac{\underline{P}_{\alpha 1}}{m_\alpha} - \frac{\underline{P}_{\beta 1}}{m_\beta} \right| b\, db\, d\varepsilon\, d^3 P_{\beta 1} \end{aligned} \tag{231d}$$

$$J_{2\alpha\beta} = \sigma_{\alpha\beta}\, g_0^{(2)}(\sigma_{\alpha\beta}) \int \cdots \int \Big[\bar{f}^{(1)}(\underset{\sim}{R}_{\alpha 1}, \underset{\sim}{P}_{\alpha 1} - \Delta \underset{\sim}{P}_{\alpha 1}; t)\, \underset{\sim}{K} \cdot \nabla_{R_{\alpha 1}} \bar{f}^{(1)}(\underset{\sim}{R}_{\alpha 1}, \underset{\sim}{P}_{\beta 1} - \Delta \underset{\sim}{P}_{\beta 1}; t)$$

$$+ \bar{f}^{(1)}(\underset{\sim}{R}_{\alpha 1}, \underset{\sim}{P}_{\alpha 1}; t)\, \underset{\sim}{K} \cdot \nabla_{R_{\alpha 1}} \bar{f}^{(1)}(\underset{\sim}{R}_{\alpha 1}, \underset{\sim}{P}_{\beta 1}; t) \Big] \cdot \left| \frac{P_{\alpha 1}}{m_\alpha} - \frac{P_{\beta 1}}{m_\beta} \right| b\, db\, d\varepsilon\, d^3 P_{\beta 1} \tag{231e}$$

In Eq. (231), $g_0^{(2)}(\sigma_{\alpha\beta})$ is the pair correlation function evaluated at the point of contact when the pair separation is just the ion-core diameter $\sigma_{\alpha\beta}$ (and therefore because of Assumptions (2) and (3) we may take $\sigma_{\alpha\alpha} = \sigma_{\alpha\beta} = \sigma_{\beta\beta} = \sigma$, b is the impact parameter and ε the azimuthal angle specifying the binary rigid-core encounter, $\underset{\sim}{K}$ a unit vector along the line of centers at the point of closest approach, and $\underset{\sim}{R}_{\alpha 1}$, $\underset{\sim}{P}_{\alpha 1}$, m_α as usual the position, momentum, and mass of particle $\alpha 1$. The equations as written neglect the possibility of a collision between like ions and are therefore consistent with Condition (3) cited above. The friction constants, ζ_{ij} $(ij = \alpha, \beta)$ are defined in terms of the autocorrelation function of the soft part of the force, ${}^{s}\underset{\sim}{F}_{\alpha\beta}$

$$\zeta_{\alpha\beta} = 3kT\tau^{-1} \int_{0+}^{\tau} ds \int_{-s}^{0+} ds' \; {}^{s}\underset{\sim}{F}_{\alpha\beta}\, {}^{s}\underset{\sim}{F}_{\alpha 1} \left[\underset{\sim}{R}_{\alpha}^{0} + (s+s') \frac{\underset{\sim}{P}_{\alpha 1}}{m_\alpha} \right] \frac{\bar{f}^{(N)}}{\bar{f}^{(1)}(\alpha 1)} \tag{232}$$

$$\times\, \delta(\underset{\sim}{R}_{\alpha 1} - \underset{\sim}{R}_{\alpha 1}^{0})\, \delta(\underset{\sim}{P}_{\alpha 1} - \underset{\sim}{P}_{\alpha 1}^{0})\, d^3R^{(N)} d^3p^{(N)}$$

and the averaging is to be performed in a canonical ensemble with the position of particle $\alpha 1$ specified. The soft force acting on a particle is then the sum of two terms, $^{(1)}\langle {}^{s}\underline{F}_{\alpha} \rangle^{\circ}$, the average total intermolecular soft force acting on a molecule at $\underline{R}_{\alpha}^{\bullet}$ when the average is performed over all other molecules in a canonical ensemble, and $^{(1)}\underline{F}_{\alpha}^{+}$, a force arising from the departure of the relative pair distribution function, $\bar{f}^{(N)}/\bar{f}^{(2)}$ from its equilibrium value.

The integro-differential equation for $\bar{f}^{(1)}(\alpha 1)$ can be solved by a variation method first proposed by Curtiss and Hirschfelder. The solution is for

$$\bar{f}^{(1)}(\alpha 1) = \bar{f}_{0}^{(1)}(\alpha 1)\Bigg\{ 1 + \left(\frac{2KT}{m_{\alpha}}\right)^{1/2} \frac{\frac{15}{4}\left[\frac{v_{\alpha}}{g_{0}^{(2)}(\sigma_{\alpha\beta})} + \frac{2}{5}\pi\sigma_{\alpha\beta}^{3}\right]\left(\frac{5}{2} - W_{\alpha 1}^{2}\right)\underline{W}_{\alpha 1}\cdot\nabla_{R_{\alpha 1}}\ln T}{\left[4\Omega_{\alpha 1}^{(2,2)} + \frac{45}{4}\left(v_{\alpha}/m_{\alpha}(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})\right)\right]}$$

$$- 5v_{\alpha}\frac{\left[\frac{1}{g_{0}^{(2)}(\sigma_{\alpha\beta})} + \frac{2\pi\sigma_{\alpha\beta}^{3}}{v_{\alpha}}\right]\left(\underline{W}_{\alpha 1}\underline{W}_{\alpha 1} - \frac{1}{3}W_{\alpha 1}^{2}\underline{\underline{U}}\right)}{\left[4\Omega_{\alpha 1}^{(2,2)} + \left[5v_{\alpha}/m_{\alpha}g_{0}^{(2)}(\sigma_{\alpha\beta})(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})\right]\right]} : \nabla_{R_{\alpha 1}}\underline{u} \qquad (233)$$

with v_{α} the volume per particle α, $\underline{W}_{\alpha 1}$ the reduced peculiar velocity equal to $(m_{\alpha}/2KT)^{1/2}\left[\frac{1}{m_{\alpha}}\underline{p}_{\alpha 1} - \underline{u}\right]$, $\underline{u}$ the mean velocity of the fluid, and $\Omega_{\alpha 1}^{(2,2)}$ the rigid-core collision cross section which is equal to $(4\pi KT/m_{\alpha})^{1/2}\sigma_{\alpha\beta}^{2}$. As usual, the unit tensor is denoted by $\underline{\underline{U}}$. We assume that $g_{0}^{(2)}(\sigma_{\alpha\beta})$ is known from equilibrium studies.

3. Mobility of Positive and Negative Ions in an Ideal Ionic Melt

The transport equation that we have derived in the Appendix and presented in Section 2 can be written in an extended form suitable to the description of the ideal ionic melt in an electric field $\underline{E}$, where the field is taken to be in the z direction. We find

$$\underline{E} = E_z \, \underline{h} \tag{234}$$

$$\frac{\partial \bar{f}^{(1)}(\alpha 1)}{\partial t} + \frac{1}{m_\alpha} \underline{p}_{\alpha 1} \cdot \nabla_{R_{\alpha 1}} \bar{f}^{(1)}(\alpha 1) + q_\alpha \underline{E} \cdot \nabla_{p_{\alpha 1}} \bar{f}^{(1)}(\alpha 1) + \underline{F}^{*}_{\alpha 1} \cdot \nabla_{p_{\alpha 1}} \bar{f}^{(1)}(\alpha 1)$$

$$= J_{1\alpha\beta} + J_{2\alpha\beta} + (\zeta_{\alpha\alpha} + \zeta_{\alpha\beta}) A^{(1)}_{\alpha 1} \bar{f}^{(1)}(\alpha 1) \tag{253}$$

There are two such equations: one for the cations and one for anions. In a static electric field, after a sufficient time t (t > momentum relaxation time of the melt) has passed,

$$\frac{\partial \bar{f}^{(1)}(\alpha 1)}{\partial t} = \frac{\partial \bar{f}^{(1)}(\beta 1)}{\partial t} = 0$$

We assume that because of strict electroneutrality, there are no configurational gradients in $\bar{f}^{(1)}(\alpha 1)$. Equation (6) then assumes the form

$$q_\alpha \underset{=}{E} \cdot \nabla_{p_{\alpha 1}} \bar{f}^{(1)}(\alpha 1) + \underset{\sim}{F}_{\alpha 1}^{*} \cdot \nabla_{p_{\alpha 1}} \bar{f}^{(1)}(\alpha 1)$$
$$= J_{1\alpha\beta} + J_{2\alpha\beta} + \frac{(\zeta_{\alpha\alpha} + \zeta_{\alpha\beta})}{m_\alpha} \mathcal{Q} \bar{f}^{(1)}(\alpha 1) \tag{236}$$

with

$$\mathcal{Q} = m_\alpha A_{\alpha 1}^{(1)} \tag{237}$$

Combining Eqs. (234) and (236) and assuming that $\underset{\sim}{F}_{\alpha 1}^{*}$ is nonzero by virtue of distortions induced by the external field, we have

$$\left\{ \frac{q_\alpha E_z + (\underset{\sim}{F}_{\alpha 1}^{*})_z}{m_\alpha} \right\} \frac{\partial \bar{f}^{(1)}(\alpha 1)}{\partial w} = J_{1\alpha\beta} + J_{2\alpha\beta}$$
$$+ \frac{(\zeta_{\alpha\alpha} + \zeta_{\alpha\beta})}{m_\alpha} \mathcal{Q} \bar{f}^{(1)}(\alpha 1) \tag{238}$$

To first order in the perturbation, the mobility of the positive ion may be calculated with the momentum distribution of the negative ions taken as locally Maxwellian. Thus if we are considering α_1 ions,

$$\left. \begin{aligned} \bar{f}^{(1)}(\alpha 1) &= \bar{f}_0^{(1)}(\alpha 1) [1 + \Phi_\alpha] \\ \bar{f}^{(1)}(\beta 1) &= \bar{f}_0^{(1)}(\beta 1) \end{aligned} \right\} \tag{239}$$

After insertion of Eq. (239) into $J_{1\alpha\beta}$ we find

$$J_{1\alpha\beta} = g_0^{(2)}(\sigma_{\alpha\beta}) \int \cdots \int \bar{f}_0^{(1)}(\alpha 1) \bar{f}_0^{(1)}(\beta 1) \left[\Phi'_{\beta 1} + \Phi'_{\alpha 1} - \Phi_{\beta 1} - \Phi_{\alpha 1} \right] d\Omega_{\beta 1} . \tag{240}$$

But $\Phi_{\beta 1} = \Phi'_{\beta 1} = 0$ in this approximation, so that

$$J_{1\alpha\beta} = g_0^{(2)}(\sigma_{\alpha\beta}) \int \cdots \int \bar{f}_0^{(1)}(\alpha 1) \bar{f}_0^{(1)}(\beta 1) \left[\Phi_{\alpha 1} - \Phi'_{\alpha 1} \right] d\Omega_{\beta 1} . \tag{241}$$

It is convenient to define an operator $J'_{\alpha\beta}$ by the relation

$$J'_{\alpha\beta} \phi = \frac{1}{\rho_\beta} \int \cdots \int \bar{f}_0^{(1)}(\beta 1) \left[\phi - \phi' \right] d\Omega_{\beta 1} \tag{242}$$

whereupon

$$J_{1\alpha\beta} = - \rho_\beta \, g_0^{(2)}(\sigma_{\alpha\beta}) \bar{f}_0^{(1)}(\alpha 1) \, J'_{\alpha\beta} \Phi_{\alpha 1} . \tag{243}$$

Consider now the term $J_{2\alpha\beta}$. Curtiss[53] has shown that may be written in the form[54]

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53. C. F. Curtiss (private communication).

54. That this integral vanishes can be shown by using the existence conditions for the solution of a Fredholm integro-differential equation. The proof is obvious.

$$J_{2\alpha\beta} = g_0^{(2)}(\sigma_{\alpha\beta})\,\bar{f}^{(1)}\int\cdots\int \bar{f}_0^{(1)}(\beta 1)\,\underline{K}\cdot\left[\nabla_{R_{\beta 1}} \ln \frac{\bar{f}_0^{(1)'}(\beta 1)}{\bar{f}_0^{(1)}(\beta 1)}\right]\sigma_{\alpha\beta}\, d\Omega_{\beta 1} \tag{244}$$

which depends linearly on $\nabla_R \ln T$ and $\nabla_R \underline{u}$ both of which are identically zero for the case under study.

The last term we must examine is the Fokker-Planck contribution. We define the operator J_1 as follows:

$$J_1 \Phi_{\alpha 1} = \left(\bar{f}_0^{(1)}(\alpha 1)\right)^{-1} \mathcal{Q}_1 \bar{f}^{(1)}(\alpha 1). \tag{245}$$

Now,

$$\mathcal{Q}_1 \bar{f}^{(1)}(\alpha 1) = \frac{KT}{m_\alpha} \nabla_{C_{\alpha 1}} \cdot \left[\bar{f}_0^{(1)}(\alpha 1)\, \nabla_{C_{\alpha 1}} \Phi_{\alpha 1}\right] \tag{246}$$

whereupon

$$J_1 \phi = \left(\bar{f}_0^{(1)}(\alpha 1)\right)^{-1} \frac{KT}{m_\alpha} \nabla_{C_{\alpha 1}} \cdot \left[\bar{f}_0^{(1)}(\alpha 1)\, \nabla_{C_{\alpha 1}} \phi\right]. \tag{247}$$

Equation (238) when written in terms of these operators assumes the form

$$\left\{ \frac{q_\alpha E_z + (\underline{F}_{\alpha 1}^{*})_z}{m_\alpha} \right\} \frac{\partial \bar{f}^{(1)}(\alpha 1)}{\partial w} = -\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta}) f_0^{(1)}(\alpha 1)\, J'_{\alpha\beta}\, \Phi_{\alpha 1} \tag{248}$$

$$+ \frac{(\zeta_{\alpha\alpha} + \zeta_{\alpha\beta})}{m_\alpha} \bar{f}_0^{(1)}(\alpha 1)\, J_1\, \Phi_{\alpha 1} .$$

The inner product of two functions $\phi(C_{\alpha 1})$ and $\Psi(C_{\alpha 1})$ may be defined by the relation

$$(\phi, \Psi) = \rho_\alpha^{-1} \int \cdots \int \bar{f}_0^{(1)}(\alpha 1)\, \phi(C_{\alpha 1})\, \Psi(C_{\alpha 1})\, d^3 C_{\alpha 1} \tag{249}$$

where it must be remembered that ρ_α and ρ_β are the number densities of α and β, respectively.

It can be shown that

$$\left. \begin{aligned} (\Psi, J'_{\alpha\beta}\phi) &= (\phi, J'_{\alpha\beta}\Psi) \\ (\Psi, J_1\phi) &= (\phi, J_1\Psi) \end{aligned} \right\} \tag{250}$$

and that

$$(\phi, J'_{\alpha\beta}\phi) \geq 0 . \tag{251}$$

It is also obvious from the definitions of $\overline{J}_{\alpha\beta}'$ and J_1, and the inner product that

$$J_{\alpha\beta}'\phi = J_{\alpha\beta}'(1+\phi)\,;\quad J_1\phi = J_1(1+\phi). \tag{252}$$

From this point onward we call $J_{\alpha\beta}'$, J. If Eq. (248) is multiplied by $-\phi(C_{\alpha 1})d^3C_{\alpha 1}$ and integrated, there results the relation

$$\begin{aligned} -\left\{\frac{q_\alpha E_z + (\underline{F}_{\alpha 1}^*)_z}{m_\alpha}\right\}\int \phi(C_{\alpha 1})\frac{\partial \bar{f}^{(1)}(\alpha 1)}{\partial w}d^3C_{\alpha 1} \\ = \rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})\int \bar{f}_0^{(1)}(\alpha 1)\phi(C_{\alpha 1})d^3C_{\alpha 1} \\ - \frac{(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})}{m_\alpha}\int \bar{f}_0^{(1)}(\alpha 1)\phi(C_{\alpha 1})J_1\Phi_{\alpha 1}d^3C_{\alpha 1} \end{aligned} \tag{253}$$

Integrating the left-hand side of this equation by parts gives

$$\begin{aligned} \int \phi(C_{\alpha 1})\frac{\partial \bar{f}^{(1)}(\alpha 1)}{\partial w}d^3C_{\alpha 1} &= -\int \bar{f}^{(1)}(\alpha 1)\frac{\partial \phi(C_{\alpha 1})}{\partial \omega}d^3C_{\alpha 1} \\ &= -\rho_\alpha\left\langle \frac{\partial \phi(C_{\alpha 1})}{\partial \omega}\right\rangle \end{aligned} \tag{254}$$

where an average is defined as

$$\langle \Psi \rangle = \frac{1}{\rho_\alpha}\int \bar{f}^{(1)}(\alpha 1)\,\Psi\, d^3C_{\alpha 1}. \tag{255}$$

The integrals on the right-hand side of Eq. (253) may be manipulated using Eqs. (249)--(252). Thus

$$\begin{aligned}\int \bar{f}_0^{(1)}(\alpha 1)\,\phi(C_{\alpha 1})\,J\Phi_{\alpha 1}\,d^3C_{\alpha 1} &= \int \bar{f}_0^{(1)}(\alpha 1)\,\phi(C_{\alpha 1})\,J(1+\Phi_{\alpha 1})\,d^3C_{\alpha 1}, \\ &= \left(\phi, J(1+\Phi_{\alpha 1})\right), \\ &= \left((1+\Phi_{\alpha 1}), J\phi\right), \\ &= \int \bar{f}_0^{(1)}(\alpha 1)(1+\Phi_{\alpha 1})J\phi\,d^3C_{\alpha 1}, \\ &= \int \bar{f}^{(1)}(\alpha 1)\,J\phi\,d^3C_{\alpha 1} \\ &= \rho_\alpha \langle J\phi \rangle\end{aligned} \tag{256}$$

and so forth. It is found that

$$\int f_0^{(1)}(\alpha 1)\,\phi\,J_1\,\Phi_{\alpha 1}\,d^3C_{\alpha 1} = \rho_\alpha \langle J_1\phi \rangle, \tag{257}$$

whereby Eq. (253) simplifies to

$$\begin{aligned}&\left\{ \frac{q_\alpha E_z + (\underline{F}_{\alpha 1}^{*})_z}{m_\alpha} \right\} \rho_\alpha \left\langle \frac{\partial\phi}{\partial\omega} \right\rangle \\ &= \rho_\alpha \rho_\beta\, g_0^{(2)}(\sigma_{\alpha\beta}) \langle J\phi \rangle - \rho_\alpha \left(\frac{\zeta_{\alpha\alpha} + \zeta_{\alpha\beta}}{m_\alpha} \right) \langle J_1 \phi \rangle .\end{aligned} \tag{258}$$

The Kihara functions,[55]

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55. T. Kihara, Rev. Mod. Phys. 25, 844 (1953).

$$\Psi_\ell^{(r)} = \left(\frac{m_\alpha C_{\alpha 1}^2}{2KT} \right)^{\ell/2} P_\ell \left(\frac{\omega}{C_{\alpha 1}} \right) S_{\ell+1/2}^{(r)} \left(\frac{m_\alpha C_{\alpha 1}^2}{2KT} \right), \tag{259}$$

where the $P_\ell \left(\frac{\omega}{C_{\alpha 1}} \right)$ are Legendre polynomials and the $S_{\ell+1/2}^{(r)} (m_\alpha C_{\alpha 1}^2 / 2KT)$ are Sonine polynomials, have the property that

$$J_1 \Psi_\ell^{(r)} = \lambda_r(\ell) \Psi_\ell^{(r)}. \tag{260}$$

The Kihara functions are therefore seen to be eigenfunctions of the Fokker-Planck operator with eigenvalues $\lambda_r(\ell) = -(2r + \ell)$. They are not, however, eigenfunctions of the collision operator J. J is, however, spherically symmetric and $J\Psi_\ell^{(r)}$ can be expanded in the form

$$J \Psi_\ell^{(r)} = \sum_s a_{rs}(\ell) \Psi_\ell^{(s)}, \tag{261}$$

where

$$a_{rs}(\ell) = (\Psi_\ell^{(s)}, J\Psi_\ell^{(r)}) / (\Psi_\ell^{(s)}, \Psi_\ell^{(r)}).$$

From the recursion relations of the Sonine and Legendre polynomials, it can be shown that

$$\left(\ell+\tfrac{1}{2}\right)\left(\frac{2KT}{m_\alpha}\right)^{1/2}\frac{\partial\Psi_\ell^{(r)}}{\partial\omega} \tag{262}$$

$$= \ell\left(\ell+\tfrac{1}{2}+r\right)\Psi_{\ell-1}^{(r)} - (\ell+1)\Psi_{\ell+1}^{(r-1)}.$$

Now, if in Eq. (258) we take

$$\left\{\frac{q_\alpha E_z + (\underset{\sim}{F}_{\alpha 1}^{*})_z}{m_\alpha}\right\}\left\langle\frac{\partial\Psi_\ell^{(r)}}{\partial\omega}\right\rangle \tag{263}$$

$$= \rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})\left\langle J\Psi_\ell^{(r)}\right\rangle - \frac{(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})}{m_\alpha}\left\langle J_1\Psi_\ell^{(r)}\right\rangle$$

which can be solved by iteration. Indeed, if (263) is multiplied by $(\ell+\frac{1}{2})(2KT/m_\alpha)^{1/2}$ and (262) employed, it is found that

$$\left\{\frac{q_\alpha E_z + (\underset{\sim}{F}_{\alpha 1}^{*})_z}{m_\alpha}\right\}\times\left\{\ell\left(\ell+\tfrac{1}{2}+r\right)\left\langle\Psi_{\ell-1}^{(r)}\right\rangle - (\ell+1)\left\langle\Psi_{\ell+1}^{(r-1)}\right\rangle\right\}$$

$$= \left(\ell+\tfrac{1}{2}\right)\left(2KT/m_\alpha\right)^{1/2}\left\{\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})\left\langle J\Psi_\ell^{(r)}\right\rangle \right. \tag{264}$$

$$\left. - \frac{(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})}{m_\alpha}\left\langle J_1\Psi_\ell^{(r)}\right\rangle\right\}$$

Introducing a reduced field strength,

$$\mathcal{E} = \left(\frac{m_\alpha}{2KT}\right)^{1/2}\left\{\frac{q_\alpha E_z + (\underset{\sim}{F}_{\alpha 1}^{*})_z}{m_\alpha}\right\} \tag{265}$$

and expanding $J\Psi_\ell^{(r)}$ as in (261) and $J_1 \Psi_\ell^{(r)}$ as in (260), Eq. (264) becomes

$$\left[\ell(\ell+\tfrac{1}{2}+r)\langle\Psi_{\ell-1}^{(r)}\rangle-(\ell+1)\langle\Psi_{\ell+1}^{(r-1)}\rangle\right]\varepsilon$$

$$=(\ell+\tfrac{1}{2})\left\{\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})\sum_s a_{rs}(\ell)\langle\Psi_\ell^{(s)}\rangle\right. \tag{266}$$

$$\left.+(2r+1)\left(\frac{\zeta_{\alpha\alpha}+\zeta_{\alpha\beta}}{m_\alpha}\right)\langle\Psi_\ell^{(r)}\rangle\right\}.$$

We assume as a first step that the off-diagonal elements $a_{rs}(\ell)$ are zero, because they vanish when J is written for Maxwell molecules. We will denote the first approximation by $\langle\ \rangle_I$. In this approximation, Eq. (266) becomes

$$\left[\ell(\ell+\tfrac{1}{2}+r)\langle\Psi_{\ell-1}^{(r)}\rangle_I-(\ell+1)\langle\Psi_{\ell+1}^{(r-1)}\rangle_I\right]\varepsilon$$

$$=(\ell+\tfrac{1}{2})\left\{\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})a_{rr}(\ell)\langle\Psi_\ell^{(r)}\rangle_I\right. \tag{267}$$

$$\left.+(2r+1)\left(\frac{\zeta_{\alpha\alpha}+\zeta_{\alpha\beta}}{m_\alpha}\right)\langle\Psi_\ell^{(r)}\rangle_I\right\}.$$

Using the identity $\Psi_{\ell+1}^{(-1)}\equiv 0$ and choosing $\ell=1$ one finds for r = 0

$$\langle\Psi_0^{(0)}\rangle_I\varepsilon=\left\{\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})a_{00}(1)\langle\Psi_1^{(0)}\rangle_I\right. \tag{268}$$

$$\left.+\frac{(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})}{m_\alpha}\langle\Psi_1^{(0)}\rangle_I\right\}$$

or

$$\mathcal{E} = \left\{ \rho_\beta\, g_0^{(2)}(\sigma_{\alpha\beta})\, a_{00}(1) + \left(\frac{\zeta_{\alpha\alpha} + \zeta_{\alpha\beta}}{m_\alpha} \right) \right\} \frac{\langle \Psi_1^{(0)} \rangle_I}{\langle \Psi_0^{(0)} \rangle_I} . \tag{269}$$

But $\Psi_1^{(0)} = (m_\alpha/2KT)^{1/2} w$ and $\Psi_0^{(0)} = 1$ so that

$$\left\{ \frac{q_\alpha E_z + (\underline{F}_{\alpha 1}^*)_z}{m_\alpha} \right\} = \left\{ \rho_\beta\, g_0^{(2)}(\sigma_{\alpha\beta})\, a_{00}(1) + \left(\frac{\zeta_{\alpha\alpha} + \zeta_{\alpha\beta}}{m_\alpha} \right) \right\} \langle w \rangle_I . \tag{270}$$

Before evaluating $\underline{F}_{\alpha 1}^*$ we write down the general nth-order approximation to $\langle w \rangle$ for those who are interested in saturation effects.

The second approximation to Eq. (266) can be obtained by inserting the first approximation, $\langle \Psi_1^{(0)} \rangle_I$ into the off-diagonal term. This leads to the equation

$$\mathcal{E} = \left\{ \rho_\beta\, g_0^{(2)}(\sigma_{\alpha\beta}) \sum_{r=0}^{\infty} a_{0r}(1) \frac{\langle \Psi_1^{(r)} \rangle_I}{\langle \Psi_1^{(0)} \rangle_I} + \left(\frac{\zeta_{\alpha\alpha} + \zeta_{\alpha\beta}}{m_\alpha} \right) \right\} \langle \Psi_1^{(0)} \rangle_{II} . \tag{271}$$

The notation $\langle \Psi_1^{(r)} \rangle_I$ indicates the use of Eq. (267) to determine $\langle \Psi_1^{(r)} \rangle$. Consider the definition

$$\tilde{A}_r(\ell) = \rho_\beta\, g_0^{(2)}(\sigma_{\alpha\beta})(\ell+\tfrac{1}{2})\,a_{rr}(\ell) - (\ell+\tfrac{1}{2})\,\lambda_r(\ell)\left(\frac{\zeta_{\alpha\alpha}+\zeta_{\alpha\beta}}{m_\alpha}\right) \tag{272}$$

so that Eq. (267) can be rewritten in the form

$$\tilde{A}_r(\ell)\langle\Psi_\ell^{(r)}\rangle_I = \varepsilon\left\{\ell(\ell+\tfrac{1}{2}+r)\langle\Psi_{\ell-1}^{(r)}\rangle_I - (\ell+1)\langle\Psi_{\ell+1}^{(r-1)}\rangle_I\right\}. \tag{273}$$

Proceeding further, Kihara[55] has shown that

$$(\Psi_1^{(r)},\Psi_1^{(0)}) = \frac{8}{3}M_\beta\left[\frac{(-1)^r}{r!}(M_\beta T)^r\frac{d^r}{dT^r}\,\Omega^{(1)}(1)\right] \tag{274}$$

with the definitions

$$M_\beta = \frac{m_\beta}{m_\alpha+m_\beta}\,, \quad g = \left|\frac{\underline{P}_\alpha}{m_\alpha} - \frac{\underline{P}_\beta}{m_\beta}\right|, \tag{275a}$$

$$\Omega^{(\ell)}(r) = \pi^{1/2}\int_0^\infty \phi^{(\ell)}\,V^{2r+2}\exp(-V^2)\,dV, \tag{275b}$$

$$V = \left\{ \left[\frac{m_\alpha m_\beta}{m_\alpha + m_\beta} \right] (2KT)^{-1} \right\}^{1/2} g \tag{275c}$$

$$\phi^{(\ell)} = \int_0^\pi (1 - \cos^\ell \theta)\, g\, I(g,\theta) \sin\theta\, d\theta . \tag{275d}$$

In the case under consideration $\phi^{(\ell)}$ is proportional to g, because in a hard-sphere collision $I(g,\theta)$ is a function of θ only. Thus it is possible to define a temperature-independent cross section ${}^{+}\Omega^{(\ell)}(r)$ as

$${}^{+}\Omega^{(\ell)}(r) = T^{-1/2}\, \Omega^{(\ell)}(r) . \tag{276}$$

Now using Eq. (276) and the relation

$$a_{or}(1) = \frac{3}{2} \left[\frac{\pi^{1/2} r!}{\Gamma(r+5/2)} \right] \left(\psi_1^{(r)} , J \psi_1^{(0)} \right) \tag{277}$$

it is found that

$$w = \left\{ \frac{q_\alpha E_z + (\underset{\sim}{F}_{\alpha 1}^{*})_z}{m_\alpha} \right\} \Big/ \left[\frac{16}{3} \frac{m_\beta}{m_\alpha + m_\beta} g_0^{(2)}(\sigma_{\alpha\beta}) + \Omega \sum_{r=0}^{\infty} \frac{(b_r T)^r}{r!} \frac{d^r}{dT^r} T^{1/2} + \left(\frac{\zeta_{\alpha\alpha} + \zeta_{\alpha\beta}}{m_\alpha} \right) \right] \tag{278}$$

Consider now the term $(\underset{\sim}{F}_{\alpha 1}^{*})_z$ which is, by definition,

$$(\underset{\sim}{F}_{\alpha 1}^{*})_z = - \int\!\!\int (\nabla_{R_{\alpha 1}} V)_z \, \bar{f}^{(2|1)}(\alpha 1, \beta 1 | \alpha 1) \, d^3 R_{\beta 1} \tag{279}$$

$$= \int\!\!\int (\nabla_{R_{\alpha 1, \beta 1}} V)_z \, \bar{f}^{(2|1)}(\alpha 1, \beta 1 | \alpha 1) \, d^3 R_{\beta 1},$$

where

$$f^{(2|1)}(\alpha 1, \beta 1 | \alpha 1) = \frac{\bar{f}^{(2)}(\alpha 1, \beta 1)}{\bar{f}^{(1)}(\alpha 1)} = \frac{\rho_\alpha^2 g_0^{(2)}(\sigma_{\alpha\beta}) \exp(-\beta \phi_1(R_1)) \exp(-\beta \phi_2(R_2))}{\rho_\alpha \exp(-\beta \phi_2(R_2))}, \tag{280}$$

where $\beta = \frac{1}{KT}$. The natural reference point for the calculation of $\underset{\sim}{F}_{\alpha 1}^{*}$ is the point $\underset{\sim}{R}_{\alpha 1}$, since the distribution of matter about this point is being considered. The pair distribution function, $f^{(2)}$ refers to two points in space with the nominal external potentials $\phi(R_{\alpha 1})$ and $\phi(R_{\beta 1})$, and the distortion in the distribution function arises solely from the non-vanishing potential gradient. Thus the Taylor expansion

$$\phi(\underline{R}_{\beta 1}) = \phi(R_{\alpha 1}) + (\underline{R}_{\beta 1,\alpha 1}\cdot\nabla_{R_{\alpha 1}})\,\phi(\underline{R}_{\alpha 1}) \tag{281}$$

leads to

$$f^{(2/1)}(\alpha 1,\beta 1|\alpha 1) = \rho_\beta\, g_0^{(2)}(\underline{R}_{\beta 1,\alpha 1})\exp(-\beta\phi(R_{\alpha 1}))\exp(-\beta(\underline{R}_{\beta 1\alpha 1}\cdot\nabla_{R_{\alpha 1}})\phi(\underline{R}_{\alpha 1})) \tag{282}$$

$$= \rho_\beta^*\, g_0^{(2)}(R_{\beta 1,\alpha 1})\exp(-\beta(\underline{R}_{\beta 1,\alpha 1}\cdot\nabla_{R_{\alpha 1}})\phi(\underline{R}_{\alpha 1}))$$

where ρ_β^* is the number density of β particles at $\underline{R}_{\alpha 1}$ at which there is an external potential $\phi(R_{\alpha 1})$; i.e., $\rho_\beta^* = \rho_\beta \exp(-\beta\phi(\underline{R}_{\alpha 1}))$. Because $(\underline{R}_{\beta 1,\alpha 1}\cdot\nabla_{R_{\alpha 1}})\phi(\underline{R}_{\alpha 1}) << KT$ for all attainable laboratory fields, the last exponential in Eq. (282) may be expanded and only linear terms in retained

$$f^{(2|1)}(\alpha 1,\beta 1|\alpha 1) = \rho_\beta^*\, g_0^{(2)}(R_{\beta 1,\alpha 1})\left[1-\beta\,(\underline{R}_{\beta 1\alpha 1}\cdot\nabla_{R_{\alpha 1}})\phi(\underline{R}_{\alpha 1})\right] \tag{283}$$

$$= \rho_\beta^*\, g_0^{(2)}(R_{\beta 1,\alpha 1})\left[1-\beta q_\alpha \underline{E}\cdot\underline{R}_{\beta 1,\alpha 1}\right].$$

Substitution of Eq. (283) into Eq. (279) leads to

$$\left(\underset{\sim}{F}_{a1}^{*}\right)_z = \int\cdots\int \left(\nabla_{R_{\beta1\alpha1}} V\right)_z \rho_\beta^{*} g_0^{(2)}(R_{\beta1\alpha1}) \left[1 - \frac{q_\alpha \underline{E}\cdot R_{\beta1\alpha1}}{KT}\right] d^3R_{\beta1\alpha1}. \tag{284}$$

We notice that

$$\int\cdots\int \left(\nabla_{R_{\beta1\alpha1}} V\right)_z \, g_0^{(2)}(R_{\beta1\alpha1})\, d^3R_{\beta1\alpha1} = 0 \tag{285}$$

because the canonical average of the intermolecular force is zero. Therefore

$$\left(\underset{\sim}{F}_{a1}^{*}\right)_z = -\int\cdot\int \left(\nabla_{R_{\beta1\alpha1}} V\right)_z \rho_\beta^{*} \left[\frac{q_\alpha \underline{E}\cdot \underline{R}_{\beta1\alpha1}}{KT}\right] d^3R_{\beta1\alpha1}\ , \tag{286}$$

and from Eq. (270), we have, after using Eq. (234)

$$\frac{q_\alpha E_z}{m_\alpha}\left[1 - \frac{\rho_\beta^{*}}{KT}\int\int \left(\nabla_R V(R)\right)_z g_0^{(2)}(R)\, z\, d^3R\right]$$

$$= \langle\omega\rangle_I \left[\rho_\beta\, g_0^{(2)}(\sigma_{\alpha\beta})\, a_{00}(1) + \left(\frac{\zeta_{\alpha a}+\zeta_{\alpha\beta}}{m_\alpha}\right)\right]. \tag{287}$$

Kihara has shown that $\alpha_{oo}(1) = \frac{5}{4}\pi^{1/2}\left(\Psi_1^{(0)}, J\,\Psi_1^{(0)}\right)$ and Davis, Rice, and Meyer[11] have evaluated this integral. Using their result in Eq. (187) we find

$$(\mu_\alpha)_I = \frac{q_\alpha}{\zeta^{HC}_{\alpha\beta} + \zeta^{s}_{\alpha\alpha} + \zeta^{s}_{\alpha\beta}}\left[1 - \frac{\rho^*_\beta}{KT}\int\cdot\int (\nabla_R V(R))_z\, g_0^{(2)}(R)\, z\, d^3R\right] \tag{288}$$

where

$$\zeta^{HC}_{\alpha\beta} = \frac{8}{3}\rho_\beta\, g_0^{(2)}(\sigma_{\alpha\beta})\,\sigma^3_{\alpha\beta}\left(2\pi\mu_{\alpha\beta} KT\right)^{1/2}$$

This identification of $\zeta^{H}_{\alpha\beta}$ is given by Eq. (136) of Chapter II. Finally,

$$(\mu_\alpha)_I = \frac{q_\alpha \mathcal{D}_\alpha}{KT}\left[1 - \frac{\rho^*_\beta}{KT}\int\cdot\cdot\int (\nabla_R V(R))_z\, g_0^{(2)}(R)\, z\, d^3R\right], \tag{289}$$

and we predict a deviation from the Nernst Einstein relation.

It is interesting to note that if one chooses as the external force $\nabla_{r_1}\mu(r_1)$, and assumes that $\underline{F}^*_{\alpha 1} = 0$ then this procedure may be repeated to give, after Eq. (16) of the previous chapter is used,

$$\zeta = \zeta_{HC} + \zeta_{S}$$

where ζ is the total friction coefficient. This shows that the Rice-Allnatt equation implies this simple sum.

4. Coefficients of Shear Viscosity and Thermal Conductance

Bearman and Kirkwood[56] have derived representations of the stress tensor and flux of energy in a binary mixture in terms of the intermolecular potential and the relevant distribution functions. These expressions are basic to the discussion of the special case of the ideal ionic melt considered herein.

According to Bearman and Kirkwood, the total stress tensor may be written as the sum of two contributions: a kinetic contribution, $\underline{\underline{\sigma}}_{K}$, which arises from translational motion of the particles in the mixture, and a potential energy contribution, $\underline{\underline{\sigma}}_{v}$, which arises from the work necessary to move one particle while it is in the force field of a second particle,

$$\underline{\underline{\sigma}} = \underline{\underline{\sigma}}_{K} + \underline{\underline{\sigma}}_{v} \tag{290}$$

These contributions may be further decomposed into parts originating from the several components of the mixture. Thus

56. R. J. Bearman and J. G. Kirkwood, J. Chem. Phys. 28, 136 (1958).

$$\underset{\approx}{\sigma}_K = \sum_{n=\alpha}^{\beta} (\underset{=}{\sigma}_n)_K = -\sum_{n=\alpha}^{\beta} \sum_{j=1}^{N_n} \langle m_n [\tfrac{1}{m_n} \underset{-}{P}_{nj} - \underset{-}{u}][\tfrac{1}{m_n} \underset{-}{P}_{nj} - \underset{-}{u}] \delta(\underset{-}{R}_{nj} - \underset{-}{r}); \bar{f}^{(N)} \rangle \quad (291)$$

and

$$\underset{=}{\sigma}_v = \sum_{n=\alpha}^{\beta} (\underset{=}{\sigma}_n)_v = \frac{1}{2} \sum_{\gamma=\alpha}^{\beta} \sum_{n=\alpha}^{\beta} \rho_\gamma \rho_n \int \cdots \int \frac{\underset{-}{r}\,\underset{-}{r}}{r} \frac{dV_{\gamma n}}{dr} g_{\gamma n}^{(2)}(r_1, r) d^3 r, \quad (292)$$

where

$$\langle \alpha ; \bar{f}^{(N)} \rangle = \int \cdots \int \alpha \bar{f}^{(N)} d^3 R^{(N)} d^3 P^{(N)}. \quad (293)$$

We may evaluate the kinetic contributions immediately:

$$(\underset{=}{\sigma}_n)_K = -\int \cdots \int m_n \left(\frac{\underset{-}{P}_{n1}}{m_n} - \underset{\sim}{u} \right) \left(\frac{\underset{-}{P}_{n1}}{m_n} - \underset{\sim}{u} \right) \bar{f}^{(1)}(n1)\, d^3 P_{n1} \,. \quad (294)$$

whereupon, for a fused salt

$$\underline{\underline{\sigma}}_K = -\int\cdot\cdot\int m_\alpha\left(\frac{\underline{p}_{\alpha 1}}{m_\alpha}-\underline{u}\right)\left(\frac{\underline{p}_{\alpha 1}}{m_\alpha}-\underline{u}\right)\bar{f}^{(1)}(\alpha 1)\,d^3\underline{p}_{\alpha 1} - \int\cdot\cdot\int m_\beta\left(\frac{\underline{p}_{\beta 1}}{m_\beta}-\underline{u}\right)\left(\frac{\underline{p}_{\beta 1}}{m_\beta}-\underline{u}\right)\bar{f}^{(1)}(\beta 1)\,d^3\underline{p}_{\beta 1}\,, \tag{295}$$

Using $\bar{f}^{(1)}(\alpha 1)$ and $\bar{f}^{(1)}(\beta 1)$ as given in Eq. (4), it is found that

$$\begin{aligned}\underline{\underline{\sigma}}_K = &-\left(\rho_\alpha kT+\rho_\beta kT+\frac{5}{3}kT\frac{\left[\frac{1}{g_0^{(2)}(\sigma_{\alpha\beta})}+\frac{4}{5}\rho_\alpha\pi\sigma_{\alpha\beta}^3\right]\nabla\cdot\underline{u}}{\left[4\Omega_\alpha^{(2,2)}+5(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})/m_\alpha\rho_\alpha g_0^{(2)}(\sigma_{\alpha\beta})\right]}\right.\\ &\left.+\frac{5}{3}kT\frac{\left[\frac{1}{g_0^{(2)}(\sigma_{\alpha\beta})}+\frac{4}{5}\rho_\beta\pi\sigma_{\alpha\beta}^3\right]\nabla\cdot\underline{u}}{\left[4\Omega_\beta^{(2,2)}+5(\zeta_{\beta\beta}+\zeta_{\alpha\alpha})/m_\beta\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})\right]}\right)\underline{\underline{U}}\\ &+2\left(\frac{5}{2}kT\frac{\left[\frac{1}{g_0^{(2)}(\sigma_{\alpha\beta})}+\frac{4}{5}\pi\rho_\alpha\sigma_{\alpha\beta}^3\right]}{\left[4\Omega_\alpha^{(2,2)}+5(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})/m_\alpha\rho_\alpha g_0^{(2)}(\sigma_{\alpha\beta})\right]}\right.\\ &\left.+\frac{5}{2}kT\frac{\left[\frac{1}{g_0^{(2)}(\sigma_{\alpha\beta})}+\frac{4}{5}\pi\sigma_{\alpha\beta}^3\right]}{\left[4\Omega_\beta^{(2,2)}+5(\zeta_{\beta\beta}+\zeta_{\alpha\alpha})/m_\beta\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})\right]}\right)\underline{\underline{\varepsilon}}\end{aligned} \tag{296}$$

where

$$\underline{\underline{\varepsilon}} = \frac{1}{2}\left(\nabla\underline{u} + \nabla\underline{u}^+\right) \tag{297}$$

To evaluate the kinetic component of the shear viscosity, the kinetic stress tensor (296) is compared with the Newtonian stress tensor,

$$\underline{\underline{\sigma}} = -\left[p + \left(\tfrac{2}{3}\eta - \phi\right)\nabla\cdot\underline{u}\right]\underline{\underline{U}} + 2\eta\underline{\underline{\varepsilon}} \tag{298}$$

whereupon one easily finds the relation

$$\eta_K = \frac{5KT}{8g_0^{(2)}(\sigma)}\left(\left\{\frac{1 + \frac{4}{5}\pi\rho_\alpha g_0^{(2)}(\sigma_{\alpha\beta})\sigma_{\alpha\beta}^3}{\Omega_\alpha^{(2,2)} + 5(\zeta_{\alpha\alpha} + \zeta_{\alpha\beta})/4m_\alpha\rho_\alpha g_0^{(2)}(\sigma_{\alpha\beta})}\right\}\right. \tag{299}$$

$$\left. + \left\{\frac{1 + \frac{4}{5}\pi\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})\sigma_{\alpha\beta}^3}{\Omega_\beta^{(2,2)} + 5(\zeta_{\beta\beta} + \zeta_{\beta\alpha})/4m_\beta\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})}\right\}\right).$$

The kinetic contribution to the heat flux may be computed analogously. Bearman and Kirkwood show that the heat flux is of the form

$$\underline{J}_K = \sum_{n=\alpha}^{\beta}\sum_{j=1}^{N_n}\left\langle \tfrac{1}{2}m_n\left[\frac{\underline{p}_{nj}}{m_n} - \underline{u}\right]^2\left[\frac{\underline{p}_{nj}}{m_n} - \underline{u}\right]\delta(\underline{R}_{nj} - \underline{r});\, \bar{f}^{(N)}\right\rangle \tag{300}$$

$$= \sum_{n=\alpha}^{\beta}\int\cdots\int \bar{f}^{(1)}(n)\left(\frac{\underline{p}_{n1}}{m_n} - \underline{u}\right)^2\left(\frac{\underline{p}_{n1}}{m_n} - \underline{u}\right)d^3\underline{p}_{n1}.$$

Performing the indicated integrations, and comparing the result with the phenomenological linear law

$$\underline{J}_K = -\kappa_K\,\nabla T, \tag{301}$$

it is found that

$$\mathcal{K}_K = \frac{75K^2T}{32g_0^{(2)}(\sigma_{\alpha\beta})}\left(\left\{\frac{1+\frac{4}{5}\pi\rho_\alpha g_0^{(2)}(\sigma_{\alpha\beta})\sigma_{\alpha\beta}^3}{\Omega_\alpha^{(2,2)}+5(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})/4m_\alpha\rho_\alpha g_0^{(2)}(\sigma_{\alpha\beta})}\right\}\right.$$

$$\left.+\left\{\frac{1+\frac{4}{5}\pi\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})\sigma_{\alpha\beta}^3}{\Omega_\beta^{(2,2)}+5(\zeta_{\beta\beta}+\zeta_{\beta\alpha})/4m_\beta\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})}\right\}\right). \tag{302}$$

Consider now the intermolecular force contributions to the shear viscosity and thermal conductivity. Because of Assumptions (3) and (4) no hard-core collisions are permitted between like molecules, and only cross component contributions to the thermal conductivity and viscosity need be considered.

For rigid-core encounters, it may be shown that

$$\left(\underline{\underline{\sigma}}_\alpha(R=\sigma_{\alpha\beta})\right)_v = N_\alpha N_\beta \int\cdots\int \sigma_{\alpha\beta}\,\underline{k}\,\Delta\underline{p}_\alpha\, \bar{f}^{(2)}(\alpha,\beta)\left|\frac{\underline{p}_\alpha}{m_\alpha}-\frac{\underline{p}_\beta}{m_\beta}\right| b\,db\,d\epsilon\,d^3\underline{p}_\alpha d^3\underline{p}_\beta \tag{303}$$

where

$$\left(\underline{\underline{\sigma}}(R=\sigma_{\alpha\beta})\right)_v = \left(\underline{\underline{\sigma}}_\alpha(R=\sigma_{\alpha\beta})\right)_v + \left(\underline{\underline{\sigma}}_\beta(R=\sigma_{\alpha\beta})\right)_v \tag{304}$$

and

$$\underline{\Delta P}_\alpha = -2\mu_{\alpha\beta}\left[\underline{K}\cdot\left(\frac{\underline{P}_\alpha}{m_\alpha}-\frac{\underline{P}_\beta}{m_\beta}\right)\right]\underline{K}\,. \tag{305}$$

As in the theory of the dense rigid-sphere fluid $\bar{f}^{(2)}(\alpha,\beta)$, is approximated by the following product:

$$\bar{f}^{(2)}(\alpha,\beta) = g_0^{(2)}(\sigma_{\alpha\beta})\,\bar{f}^{(1)}(\alpha)\,\bar{f}^{(1)}(\beta) \tag{306}$$

Thus the integral to be evaluated is

$$\left(\underline{\underline{\sigma}}_\alpha(R=\sigma_{\alpha\beta})\right)_v = -2N_\alpha N_\beta \mu_{\alpha\beta}\sigma_{\alpha\beta}\int\cdots\int g_0^{(2)}(\sigma_{\alpha\beta})\,\underline{K}\cdot\left(\frac{\underline{P}_\alpha}{m_\alpha}-\frac{\underline{P}_\beta}{m_\beta}\right)\underline{K}\,\underline{K} \tag{307}$$
$$\cdot\,\bar{f}^{(1)}(\alpha)\,\bar{f}^{(1)}(\beta)\left|\frac{\underline{P}_\alpha}{m_\alpha}-\frac{\underline{P}_\beta}{m_\beta}\right| b\,db\,d\varepsilon\,d^3P_{\alpha 1}\,d^3P_{\beta 1}\,.$$

The quadratures required in Eq. (307) may be performed using well-known methods. The results, when compared to the Newtonian stress tensor, leads to the viscosity contribution

$$\left(\eta_\alpha(R=\sigma_{\alpha\beta})\right)_v = \left(\eta_\alpha^{(1)}(R=\sigma_{\alpha\beta})\right)_v + \left(\eta_\alpha^{(2)}(R=\sigma_{\alpha\beta})\right)_v \tag{308}$$

with

$$\left(\eta_{\alpha}^{(1)}(\sigma_{\alpha\beta})\right)_{v} = \left(\frac{2\pi\sigma_{\alpha\beta}^{3}KT}{15}\right)\mu_{\alpha\beta}\, g_{0}^{(2)}(\sigma_{\alpha\beta})\rho_{\alpha}\rho_{\beta}$$

$$\times\left[\frac{5}{m_{\alpha}\rho_{\alpha}}\frac{\left[\frac{1}{g_{0}^{(2)}(\sigma_{\alpha\beta})}+\frac{4\pi\rho_{\alpha}\sigma_{\alpha\beta}^{3}}{15}\right]}{\left[4\Omega_{\alpha}^{(2,2)}+\frac{5(\zeta_{\alpha\alpha}+\zeta_{\alpha\beta})}{m_{\alpha}\rho_{\alpha}g_{0}^{(2)}(\sigma_{\alpha\beta})}\right]} + \frac{5}{m_{\beta}\rho_{\beta}}\frac{\left[\frac{1}{g_{0}^{(2)}(\sigma_{\alpha\beta})}+\frac{4\pi\rho_{\beta}\sigma_{\alpha\beta}^{3}}{15}\right]}{\left[4\Omega_{\beta}^{(2,2)}+\frac{5(\zeta_{\beta\beta}+\zeta_{\beta\alpha})}{m_{\beta}\rho_{\beta}g_{0}^{(2)}(\sigma_{\alpha\beta})}\right]}\right] \tag{309}$$

$$\left(\eta_{a}^{(2)}(\sigma_{\alpha\beta})\right)_{v} = \left(\frac{4\pi\sigma_{\alpha\beta}^{3}}{15}\right)\rho_{\alpha}\rho_{\beta}\, g_{0}^{(2)}(\sigma_{\alpha\beta})\left(\frac{2\mu_{\alpha\beta}KT}{\pi}\right)^{1/2}. \tag{310}$$

Similarly, Bearman and Kirkwood give the heat flux due to the intermolecular force in the form

$$\underset{\sim}{J}_{v} = \sum_{n=a}^{\beta}\sum_{m=a}^{\beta}\frac{1}{2}\int\cdots\int\left\{V_{nm}(r)\,\underline{\underline{U}} - \frac{\underline{r}\,\underline{r}}{r}V_{nm}'(r)\right\} \cdot\left[\underset{\sim}{\dot{j}}_{nm}^{(2)} - \rho_{nm}^{(2)}(r_{1},r)\,\underset{\sim}{u}\right]d^{3}r. \tag{311}$$

where $\rho_{nm}^{(2)}(r_{1},r)$ is the average number density of molecules of type n at r_1 and m at r in the configuration space of ordered pairs of molecules, and $\underset{\sim}{\dot{j}}_{nm}^{(2)}$ is the particle current density in pair space (6 dimensions).

With Assumptions (3) and (4), Eq. (309) is reduced to

$$\underset{\sim}{J}_v(\sigma) = \iint \left[V_{\alpha\beta}(r)\underset{\approx}{U} - \frac{\underset{\approx}{rr}}{r} V'_{\alpha\beta}(r) \right] \cdot \left[\underset{\sim}{j}^{(2)}_{\alpha\beta} - \rho^{(2)}_{\alpha\beta}(r_1, r) \right] d^3 r. \tag{312}$$

This is precisely the result of Irving and Kirkwood, and we may proceed in our analysis exactly as have Rice, Kirkwood, Ross and Zwanzig. After carrying through all the integrations, it is found that

$$\left(K_\alpha(\sigma_{\alpha\beta}) \right)_v = \left(K^{(1)}_\alpha(\sigma_{\alpha\beta}) \right)_v + \left(K^{(2)}_\alpha(\sigma_{\alpha\beta}) \right)_v \tag{313}$$

with

$$\left(K^{(1)}_\alpha(\sigma_{\alpha\beta}) \right)_v = \frac{60\pi\sigma_{\alpha\beta}^3 \rho_\alpha \rho_\beta k^2 T g_0^{(2)}(\sigma_{\alpha\beta})}{9(m_\alpha + m_\beta)} \Big[(5x^3 - 7x^2 + 11x - 9) A'_\alpha$$

$$+ (7x^2 - 10x + 5) A'_\beta \Big],$$

$$A'_\alpha = \frac{15}{4} \frac{\frac{1}{\rho_\alpha g_0^{(2)}(\sigma_{\alpha\beta})} + \frac{2\pi\sigma_{\alpha\beta}^3}{5}}{4\Omega_\alpha^{(2,2)} + \frac{45}{4}\frac{(\zeta_{\alpha\alpha} + \zeta_{\alpha\beta})}{m_\alpha \rho_\alpha}},$$

$$A'_\beta = \frac{15}{4} \frac{\frac{1}{\rho_\beta g_0^{(2)}(\sigma_{\alpha\beta})} + \frac{2\pi\sigma_{\alpha\beta}^3}{5}}{4\Omega_\beta^{(2,2)} + \frac{45}{4}\frac{(\zeta_{\beta\beta} + \zeta_{\beta\alpha})}{m_\beta \rho_\beta}},$$

$$x = \frac{m_\alpha}{m_\alpha + m_\beta} \tag{314}$$

$$\left(K_{\alpha}^{(2)}(\sigma) \right)_{v} = \rho_{\alpha}\rho_{\beta} g_{0}^{(2)}(\sigma_{\alpha\beta}) \left(\frac{4\pi\sigma_{\alpha\beta}^{3}}{3} \right) \left(\frac{2\mu kT}{\pi} \right)^{1/2} \frac{k\,\sigma_{\alpha\beta}}{m_{\alpha}+m_{\beta}} , \tag{315}$$

There now remains only the computation of the soft short range potential contribution to the energy flux and momentum flux. In the Bearman-Kirkwood formalism, the soft-force contribution to the shear tensor is

$$\sigma_{v}(R > \sigma_{\alpha\beta}) = \frac{1}{2} \sum_{n=\alpha}^{\beta} \sum_{m=\alpha}^{\beta} \rho_{n}\rho_{m} \int \cdot \cdot \int \frac{\mathbf{r}\mathbf{r}}{r} \frac{dV_{nm}^{s}(r)}{dr} g_{nm}^{(2)}(r_{1}, r) d^{3}r . \tag{316}$$

Consider now the implications of the assumptions defining an ideal ionic melt. In Assumption (5) we have stated that the short-range soft forces are much more important than the Coulomb potential in transport phenomena. Rice has shown that the Coulombic contribution to the molecular friction coefficient is negligibly small. Thus in the soft-force contribution to the stress tensor and heat flux, we consider the soft short-range forces to be the only important soft forces. These forces have a range which is less than two molecular diameters. It is therefore consistent to remark that only nearest-neighbor soft-force interactions are important. But from Assumption (3) an ion is surrounded by ions of opposite charge. Equation (312) therefore reduces to

$$\sigma_V (R > \sigma_{\alpha\beta}) = \rho_\alpha \rho_\beta \int \cdots \int \frac{\mathbf{r}\mathbf{r}}{r} V^{s\,\prime}_{\alpha\beta}(r)\, g_0^{(2)}(\mathbf{r}_\alpha, \mathbf{r}_{\alpha\beta})\, d^3 r_{\alpha\beta} . \tag{317}$$

We refer the reader to the paper by Lowry and Rice for the details of the calculation of the soft contribution to the shear viscosity.

The same procedure may be followed in evaluating the sofr contribution to the thermal conductivity. The heat flux is also given by Eq. (8) but now for $R > \sigma_{\alpha\beta}$. We refer the reader to the paper of Ikenberry and Rice for the details of the calculation of the thermal conductivity.

As a result of applying the procedures detailed by Ikenberry, and Rice and Lowry and Rice, the following contributions to the thermal conductance and shear viscosity are obtained:

$$\eta_V (R > \sigma_{\alpha\beta}) = \frac{\pi(\zeta_{\alpha\alpha} + 2\zeta_{\alpha\beta} + \zeta_{\beta\beta})}{15kT} \int_0^\infty R^3 V'(R)\, g_0^{(2)}(R)\, \psi_2(R)\, dR \tag{319}$$

$$\frac{d}{dR}\left(R^2 g_0^{(2)}(R)\frac{d\Psi_2(R)}{dR}\right) - 6g_0^{(2)}(R)\Psi_2(R) = R^2\frac{d}{dR}g_0^{(2)}(R), \tag{320}$$

$$\lim_{R\to\sigma} R^2 g_0^{(2)}(R)\frac{d\Psi_2(R)}{dR} = 0,$$

$$\lim_{R\to\infty} \Psi_2(R) = 0.$$

$$K_v(R>\sigma) = \frac{\pi KT\rho_\alpha\rho_\beta}{3(\zeta_{\alpha\alpha}+2\zeta_{\alpha\beta}+\zeta_{\beta\beta})}\int_{\sigma_{\alpha\beta}}^{\infty} R^2[RV'(R)-V(R)]\,g_0^{(2)}(R)\frac{d}{dR}\left[\frac{\partial \ln g_0^{(2)}(R)}{\partial T}\right]dR \tag{321}$$

$$+\frac{\pi KT\rho_\alpha\rho_\beta}{(\zeta_{\alpha\alpha}+2\zeta_{\alpha\beta}+\zeta_{\beta\beta})}\int_{\sigma_{\alpha\beta}}^{\infty}[R^2V(R)-R^3V'(R)]\frac{\partial}{\partial T}g_0^{(2)}(R)\,dR.$$

Of course, the total thermal conductance and shear viscosity have the respective forms

$$\eta = \eta_K + \eta_V(\sigma_{\alpha\beta}) + \eta_V(R>\sigma_{\alpha\beta}), \tag{322}$$

$$K = K_K + K_V(\sigma_{\alpha\beta}) + K_V(R>\sigma_{\alpha\beta}). \tag{323}$$

5. Discussion

It can be seen from the preceding analysis that the properties of a molten salt should be very mcuh like the properties of a simple dense fluid. Detailed calculation must await the determination of accurate pair correlation functions and non-Coulombic contributions to the interionic pair potential. However one property unique to the molten salt, its electrical conductivity, deserves some further attention here even though calculations are hindered by lack of adequate input information.

In Eq. (289) we have displayed a relationship between the mobility of a charge carrier and the interaction potential. There is predicted to be a deviation from the Nernst-Einstein relations due to the distortion from spherical symmetry of the surroundings of a selected ion. Because of this distortion there is an internal electric field exerted on the selected ion which is opposed (antiparallel) to the external field. Since the net field exerted on an ion is less than the applied field, the diffusion mobility is expected to exceed the conductance mobility. This effect has been observed many times but no adequate interpretation has heretofore been advanced. The most common model assumes ion pairing such that the neutral pairs contribute to diffusion but not to electrical conductance. We shall see that such an assumption is unnecessary.

From Eq. (289) the deviation term is found to be

$$\Delta = \frac{2\pi\rho_A}{3KT}\int_{\sigma}^{\infty}\left(\frac{\partial V}{\partial R}\right)R^3 g_0^{(2)}(R)\,dR \tag{324}$$

after integration over the angles of a spherical coordinate system with z chosen to be the polar axis. It will be noted that the integral in Δ is identical to the integral defining the pressure in a simple fluid Eq. (214) and the calculation is therefore very sensitive to the relative positions of the minimum of V and the first peak of $g_0^{(2)}(R)$. Calculation of Δ requires that V and $g_0^{(2)}$ be known. To estimate the magnitude of Δ we assume that $g_0^{(2)}(R)$ is the same as that for liquid Ar at the same number density,[57] and that the potential is of a depth determined by the ionization potentials and polarizabilities of the ions but scaled to the depth of the Ar-Ar potential. This procedure leads to $\varepsilon = 96 \times 10^{-16}$ ergs compared to $\varepsilon = 171 \times 10^{-16}$ ergs. While these approximations are admittedly crude, no better potentials or radial distribution functions are currently available. In the simplest estimate we put $g_0^{(2)}(R) = 1$ for all $\frac{R}{\sigma_{\alpha\beta}} \geq 1$, and $g_0^{(2)} = 0$ for $\frac{R}{\sigma_{\alpha\beta}} < 1$. This leads to $\Delta = 0.48$ at 1100°K for KCl using the 6-12 potential with parameters $\varepsilon = 96 \times 10^{-16}$ ergs and

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57. By the same density is meant a density corresponding to the Kirkwood parameter = 20, in the Kirkwood solution of the Born-Green integro-differential equation.

$\sigma = 3.14 \times 10^{-8}$ cm. This is certainly a crude value of Δ because $g_0^{(2)}$ rises appreciably above unity in the first peak and it is just this region of the integrand that contributes heavily to Δ. However, because of the opposite signs of the attractive and repulsive forces, it is not clear whether or not this value of Δ is large or small. For a better but still crude calculation we use the function $g_0^{(2)}$ relevant to liquid Ar at the constant density 1.68×10^{22} cm^{-3} and for several different temperatures and pressures.[58] This integration leads to $\Delta \approx 0.28$-0.30 a value sensibly independent of the variations in $g_0^{(2)}$ over the range studied. For Ar, these variations correspond to the temperatures 128^o, 133.5^o and 185.5^oK with pressures of 50, 100, and 500 atm, all at the constant density cited.

The predicted deviations from the Nernst-Einstein relation are of the order of 10% to 40%, a range which is in agreement with the experimental date presently available. (See Table 6). Clearly, the calculation of a precise value of Δ will require much more accurate pair potentials and pair correlation functions than have been used in this crude computation. Nevertheless, the order of magnitude agreement strongly suggests that no ion pairing need be invoked in the description of simple molten salts far from the critical temperature.

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58. In our computation, the value of the integral was found from the equation of state of liquid argon at the temperatures reported and does not contain the errors of the Kirkwood theory of the pair correlation function.

Table 6

Experimental Deviations from Nernst-Einstein Relation in Molten Salts

Salt	Temperature ^{o}K	Diffusion coefficient $\times 10^4$ cm^2/sec From Ion Mobility	From Tracer Differential	$-\Delta$
NaCl	1111	1.39	1.63	0.17
	1250	1.82	2.47	0.36
RbCl	1010	0.75	0.88	0.17
	1163	0.17	1.46	0.24
CsCl	943	0.60	0.73	0.21
	1063	0.93	1.15	0.23
NaI	943	1.05	1.13	0.08
	1067	1.44	1.47	0.014

The characteristic simplifying features of the ideal ionic melt studied in this chapter have also been recognized and successfully exploited in several recent theoretical studies of molten salts. On the basis of an earlier calculation it has been asserted that the Coulomb potential plays no role in dissipation of momentum and energy except that of determining the local structure of the liquid. Recent calculations of the thermodynamic properties of salt mixtures[59] and of pure salts indicate that the compressibility[60] and equation of state[61] of an ionic melt are well represented in terms of a hard-sphere fluid model. Again, the only role of the long-range Coulomb potential is to determine the density and local structure of the liquid. Indeed, it appears that many of the properties of ordinary liquids are well approximated by a model in which the attractive forces determine the volume of the liquid, but all dynamic properties are determined by hare-core encounters. This suggests that the statistical geometry of the rigid-sphere fluid is very similar to that of a real liquid, an idea exploited by Reiss and co-workers.[62] We believe this to be a very good approximation for many (but not all) of the properties of an ionic fluid.

It is important to examine the range in which the theory presented here may be expected to be valid. It is well known that when alkali halide melts or other ionic melts vaporize, the gaseous state is composed of molecules not ions. Thus, as the density of the fluid is lowered there must be a transition from a fluid of ions to a fluid of molecules, i.e., extensive ion pairing and molecule formation must occur. For this reason the theory of ideal ionic melts, which is based on a reference

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59. H. Reiss, J. L. Katz, and O. J. Kleppa, J. Chem. Phys. 36, 144 (1962).

60. F. H. Stillinger, J. Chem. Phys. 35, 1581 (1961).

61. D. A. McQuarrie, J. Phys. Chem. 66, 1508 (1961).

62. H. Reiss and J. Mayer, J. Chem. Phys. 34, 2001 (1961).

state in which all particles are ions, will be valid at high densities and for temperatures far from the critical temperature. A complete theory, which of necessity would include the possibility of molecule formation, would not need different forces since the alkali halide molecules are known to be "ionic". However, to develop such a theory the phase space of the system would have to include those regions corresponding to bound states. It is difficult to make a precise description of this phase space, and those descriptions which have been given[63] are awkward to work with. For the present it seems best to examine the properties of molten salts far from the critical point with the intent of testing in detail the extent theory. From such studies may come the clues needed for definitive extension of the theory of the lower density region of the fluid range.

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63. T. L. Hill, Statistical Mechanics (McGraw-Hill Book Company, Inc., New York, 1956).

CHAPTER IV

A NON-MARKOVIAN THEORY FOR MOMENTUM RELAXATION

1. Introduction

Recently, Rahman[65] has performed some very interesting computer calculations. He studied the classical equations of motion of 864 argon atoms interacting with a Lennard-Jones potential, to simulate molecular dynamics in liquid argon at 94.4°K and a density of 1.374 gm/cm^3. The basic assumptions made are that a) classical mechanics is valid and b) argon atoms interact through a two body central force. Further assumptions have to be made to make the calculation possible. The two body potential has to be truncated beyond a certain range, the number of particles in the assembly has to be kept small, and suitable boundary conditions must be imposed. Finally, the classical equations of motion are written as a set of difference equations, thus involving a finite increment of time for the transition from one set of positions and velocities to another set. These difference equations are then solved on a CDC 3600.

Rahman computes the space time self-correlation function, the velocity autocorrelation function, and the spectrum

65. A. Rahman, private communication.

associated with this autocorrelation function among other things. Although his original goal was to study the Van Hove space time correlation functions and thereby to predict the way in which slow neutrons would be inelastically scattered from the liquid, Rahman has actually performed an "experiment" and we shall regard his calculations as raw data which require theoretical explanation.

In recent years great progress has been made in the development of a general statistical mechanics of irreversible processes. The work of Van Hove[66-68] and Prigogine and co-workers[1,2] stands in the forefront of these efforts. The formalism developed has been successfully used to derive the well known kinetic equations, such as the Boltzmann equation and the Fokker-Planck equation. All of these derivations are carried out for dilute or weakly coupled systems and, to date, no kinetic equations for dense or strongly coupled systems have been derived by these methods. There have been some attempts to derive the Rice-Allnatt equation on the basis of these methods, but nobody has succeeded. Furthermore, although the theory is exact within the limits of perturbation theory and provides a method for deriving non-Markovian equations, there has been very little activity in this area. To understand, and explain such properties of dense fluids, as the velocity

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66. L. Van Hove, Physica 21, 512 (1955).
67. L. Van Hove, Physica 22, 343 (1956).
68. L. Van Hove, Physica 23, 441 (1957).

and force autocorrelation functions, a realistic non-Markovian kinetic equation for dense strongly coupled systems is absolutely necessary. Because Prigogine's analysis is based on a perturbation solution of the Liouville equation in which the free particle states are chosen as the basis set, it seems reasonable to doubt that such a realistic equation will be found. If the Liouville equation could be solved for a more realistic system; that is, a system which contains some of the features of the dense fluid, there might be some hope for obtaining the much needed non-Markovian equation. Thus, due to the lack of information the scientist interested in the statistical features of simple dense fluids must adopt methods which are questionable from the point of view of rigor. To be rigorous is indeed desirable, but for the present problem impossible. The work presented in this chapter is therefore based on an ansatz, the validity of which will be tested on the basis of whether or not it provides agreement with the computer experiment of Rahman.

Recently Zwanzig[69] has derived the autocorrelation formulae for transport coefficients. The first part of his paper was devoted to a derivation of these formulae based on the classical work of Kubo, Yokata, and Nakajima[8] in which linear regression of fluctuations is assumed. In addition, these authors regard the fluctuating variables as a multidimensional Markov random process. It is well known that this

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69. R. Zwanzig, J. Chem. Phys. 40, 2527 (1964).

derivation leads to a contradiction which may be simply stated; the autocorrelation function of a random variable at $t = 0$ is equal to its first derivative with respect to time at $t = 0$. The function at $t = 0$ is nonzero, whereas its derivative at $t = 0$ is zero. Hence, the contradiction. Zwanzig makes the assumption of linear regression but does not find it necessary to make the Markovian assumption. By introducing a parameter of slowness ξ in such a way that as $\xi \to 0$ the product ξt is held fixed, that is in such a way that as $\xi \to 0$, $t \to \infty$, Zwanzig obtains the Markovian equation for the regression of fluctuations as well as the Kubo formula. He then concludes that for short times the non-Markovian nature of the molecular process cannot be ignored, but for long times these effects become less important. The contradiction mentioned above therefore does not appear in Zwanzig's derivation, because according to him it is absurd to think that a Markovian equation holds for short times. To illustrate his method, Zwanzig derives Kirkwood's formula for the friction coefficient, a very interesting result indeed.

Starting with Onsager's pioneering work,[70,71] almost all transport theories have been based on Markovian assumptions.[72] In the context of the work to be outlined here these assumptions may be states: the autocorrelation function of the

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70. L. Onsager, Phys. Rev. 40, 405 (1931).

71. L. Onsager, Phys. Rev. 37, 2265 (1931).

72. S.R. DeGroot and P. Mazur, Non-Equilibrium Thermodynamics (North-Holland Publishing Company, Amsterdam, 1962).

momentum should decay to zero long before a molecule can be said to have moved a macroscopic distance. Of course in this time neighboring molecules cannot move a macroscopic distance, and the local density should remain fairly constant. This assumption, it may be pointed out, makes behavior in momentum space independent of behavior in configuration space, that is, it decouples momentum and configuration space. What happens if the density fluctuates while the momentum correlation function is decaying? That is, what if hydrodynamic times are of the same order of magnitude as the time scale on which molecular processes such as momentum relaxation take place? This is a question which is ignored by use of the Markovian assumption.

By introducing a parameter of slowness ξ , and by letting $\xi \to 0$, Zwanzig essentially forces the density to remain constant while the momentum is relaxing. It is thus no surprise that he obtains a Markovian result. As we have said, letting $\xi \to 0$ is tantamount to letting $t \to \infty$. Thus for long time behavior the decay of the momentum should be Markovian. This can be said more clearly in the following way. For long time behavior the decay of a Fourier component of the density may be found from the space Fourier transform of the diffusion equation,

$$\frac{\partial \rho_k}{\partial t} = -k^2 \mathcal{D} \rho_k .$$

The diffusion equation describes the asymptotic time evolution of the Fourier components of the density. The individual Fourier components of the density decay at different rates depending upon the wavelength of the inhomogeneity or density fluctuation $\frac{1}{k}$. In any case the rate of change of the Fourier components decreases with time; that is as $t \to \infty$ $\frac{\partial \rho_k}{\partial t} \to 0$. Thus for long periods of time a particle on the average sees and feels a fairly constant background, a background with density changing very slowly in time. For small k, or large wavelength, fluctuations in the density, $\frac{\partial \rho_k}{\partial t} \to 0$ quite slowly, and these inhomogeneities do not have a very important effect on the decay of momentum. The most important contributions to non-Markovian behavior of the momentum come from the short wavelength or large $\underline{k}$ density fluctuations, because these correspond to rapid processes.

The ansatz used in this work is that the memory the random variable has for its previous value is exponential; that is, the closer to the previous value it is in time, the better is its memory of that variable. This will be made more meaningful later.

2. Formulation of the Problem

Most discussions of fluctuations begin by assuming the regression of fluctuations. This assumption may be stated simply in the following way. Spontaneous fluctuations from thermal equilibrium obey macroscopic transport laws. As we have said, Markovian behavior is also assumed, by which we mean that the correlation time of a macroscopic random variable $\alpha(t)$ is much greater than that of its time derivative $\dot{\alpha}(t)$ i.e. $(\underline{r}(t), \underline{v}(t))$, $(\underline{v}(t), \underline{E}(t))$.

The macroscopic random variables of interest here are a set $\alpha_1(t), \alpha_2(t), \alpha_3(t), \ldots \ldots \alpha_{n-1}(t), \alpha_n(t)$. This set may be denoted by a vector $\underline{\alpha}(t)$ where it is understood that the n-tuple of numbers $\{\alpha_n(t)\}$ are the components of this vector. Macroscopic transport laws describe the evolution in time of $\bar{\underline{\alpha}}(t)$, where $\bar{\underline{\alpha}}(t)$ denotes the average of $\underline{\alpha}(t)$ in repeated experiments all performed in such a way that $\underline{\alpha}(0)$ is the same. This is a fixed ensemble average where by fixed we mean that all of the members of the ensemble are chosen in such a way that at t = 0 they all have the same value $\underline{\alpha}(0)$. The random variables are chosen as deviations in properties from their thermal equilibrium values. Such a property would be the average momentum of a particle at time t given that its initial momentum at time zero was $\underline{p}_1(0)$. Obviously this quantity is a deviation, because its thermal equilibrium value is zero.

In the Markovian form, the linear regression laws may be written as

$$\frac{d\bar{\alpha}_i(t)}{dt} = -\sum_{j=1}^{n} K_{ij}\,\bar{\alpha}_j(t). \tag{325}$$

Here the coefficients K_{ij} are independent of time. Zwanzig shows that Eq. (325) is a limiting form of the much more general non-Markovian equation

$$\frac{d\bar{a}_i(t)}{dt} = -\sum_{j=1}^{n}\int_0^t K_{ij}(t_1)\,\bar{a}_j(t-t_1)\,dt_1 \tag{326}$$

The "ansatz" mentioned in the introduction and used throughout this chapter is that

$$K_{ij}(t_1) = \alpha_{ij} K_{ij}\, e^{-\alpha_{ij} t} \tag{327}$$

We shall see later that any two parameter $K_{ij}(t_1)$ can be chosen which reduces to Eq. (325) in the Markovian limit. Thus for example

$$K_{ij}(t_1) = e^{-\alpha_{ij} t} \cos \gamma_{ij} t, \tag{328}$$

or

$$K_{ij}(t_1) = e^{-\alpha_{ij} t}\, e^{-\gamma_{ij} t^2} \tag{329}$$

might have been chosen but the analysis would have been far too difficult. Equation (327) was chosen originally for the following reason. If $t-t_1 >> \tau$, where τ is the time over which the random variables corresponding to the density fluctuations interfered with the decay of the momentum in our example in the introduction, then $\bar{\alpha}_j(t-t_1) \sim \bar{\alpha}_j(t)$ and the integration may be extended to infinity. Thus Eq. (326) becomes

$$\frac{d\bar{\alpha}_i(t)}{dt} = -\sum_{j=1}^{n}\left[\int_0^\infty K_{ij}(t_1)dt_1\right]\bar{\alpha}_j(t). \tag{330}$$

This is the Markovian limit of Eq. (326) and in order that Eq. (325) be retrieved it is necessary that

$$\int_0^\infty K_{ij}(t_1)dt_1 = K_{ij}. \tag{331}$$

It is immediately observed that the particular ansatz made in this work, that is Eq. (327) automatically satisfies this condition. Equations (328) and (329) may be forced to do so also. We can show this by a method very similar to the manner in which Zwanzig obtains the Markovian autocorrelation function formula, i.e., by introducing the parameter of slowness ξ. This shall be discussed in relation to the particular problem of the velocity correlation function.

In going from Eq. (326) to Eq. (325) via equations (330) and (331), an approximation has been made. This can be best illustrated by using an equation for one random variable instead of n. Equation (326) may be written for this situation as

$$\frac{d\bar{\alpha}(t)}{dt} = -\int_0^t K(t_1)\bar{\alpha}(t-t_1)dt_1. \tag{332}$$

The ansatz we shall use is that

$$K(t_1) = \alpha K' e^{-\alpha t_1}. \tag{333}$$

The Laplace transform $\tilde{K}(s)$ of $K(t_1)$ is introduced.

$$\tilde{K}(s) = \int_0^\infty dt_1\, e^{-st_1} K(t_1). \tag{334}$$

The inverse transform is

$$K(t_1) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} ds\, e^{st_1} \tilde{K}(s), \tag{335}$$

where c denotes the point at which the Bromwich contour should be constructed.

Substituting the ansatz of Eq. (333) into Eq. (334) yields

$$\tilde{K}(s) = \frac{\alpha K'}{\alpha + s}. \tag{336}$$

Equation (336) can now be used to verify the following results

$$\left[\frac{d}{ds} \tilde{K}(s) \right]_{s=0} + \frac{1}{\alpha^2} \operatorname{Res} \tilde{K}(-\alpha) = 0, \tag{337}$$

$$\tilde{K}(0) - \frac{1}{\alpha} \operatorname{Res} \tilde{K}(-\alpha) = 0, \tag{338}$$

where $\operatorname{Res} \tilde{K}(-\alpha)$ denotes the residue of $\tilde{K}(s)$ at its single pole $-\alpha$. Substituting Eq. (336) into Eq. (335) it is found that

$$K(t_1) = e^{-\alpha t_1} \operatorname{Res} \tilde{K}(-\alpha), \tag{339}$$

$$\int_0^\infty K(\tau) d\tau = \frac{1}{\alpha} \operatorname{Res} \tilde{K}(-\alpha), \tag{340}$$

or by Eq. (338)

$$\int_0^{+\infty} K(\tau)\,d\tau = \tilde{K}(0). \tag{341}$$

Similarly it is found that

$$\int_0^{\infty} d\tau\, K(\tau)\,\tau = -\left[\frac{d}{ds}\tilde{K}(s)\right]_{s=0} . \tag{342}$$

The identity

$$(-1)^n \frac{d^n}{d\alpha^n}\int_0^{\infty} e^{-\alpha\tau}\,d\tau = \int_0^{\infty} d\tau\,\tau^n e^{-\alpha\tau}$$

may easily be verified. Thus

$$\begin{aligned}\int_0^{\infty} d\tau\,\tau^n e^{-\alpha\tau} &= \left[(-1)^n \frac{d^n}{d\alpha^n}\right]\frac{1}{\alpha} \\ &= \frac{(-1)^{2n}}{\alpha^{n+1}}\,n! \\ &= \frac{n!}{\alpha^{n+1}}\end{aligned} \tag{343}$$

and

$$\begin{aligned}\int_0^{\infty} d\tau\,\tau^n K(\tau) &= \frac{n!}{\alpha^{n+1}}\,\mathrm{Res}\,\tilde{K}(-\alpha) = \frac{n!}{\alpha^{n+1}}\,\tilde{K}(0) \\ &= \frac{n!}{\alpha^n}\,\tilde{K}(0).\end{aligned}$$

Equation (332) may also be written

$$\frac{d\bar{\alpha}(t)}{dt} = -\int_0^t dt_1 K(t-t_1)\bar{\alpha}(t_1), \tag{344}$$

$\bar{\alpha}(t_1)$ may be expanded around t. Let $\tau = t - t_1$, then

$$\bar{\alpha}(t_1) = \sum_{n=0}^{\infty} (-1)^n \frac{\tau^n}{n!} \frac{d^n}{dt^n} \bar{\alpha}(t). \tag{345}$$

Substituting this into Eq. (344), and changing variables in the integral, it is found that

$$\frac{d\bar{\alpha}(t)}{dt} = -\sum_{n=0}^{\infty} (-1)^n \int_0^t d\tau\, K(\tau) \frac{\tau^n}{n!} \frac{d^n}{dt^n}\bar{\alpha}(t). \tag{346}$$

For $t >> \frac{1}{\alpha}$, the limit of this integral may be extended to infinity. Thus using Eq. (343) yields

$$\frac{d\bar{\alpha}(t)}{dt} = -\sum_{n=0}^{\infty} \tilde{K}(0) \frac{(-1)^n}{\alpha^n} \frac{d^n}{dt^n} \bar{\alpha}(t). \tag{347}$$

We have stated what is meant by the Markovian assumption in the first part of this chapter. There we said that the temporal variation of $\frac{d\bar{\alpha}(t)}{dt}$ is assumed to be much smaller than that of $\bar{\alpha}(t)$. Thus we may neglect all terms with $n > 1$ in this expansion. As we shall see later, α is of the same order as $\tilde{K}(0)$, and we are therefore justified in assuming that $\tilde{K}(0)/\alpha^n \sim 0$ for $n > 1$. Equation (347) becomes, after all these considerations are introduced,

$$\frac{d\bar{\alpha}(t)}{dt} = -\tilde{K}(0)\bar{\alpha}(t) + \frac{\tilde{K}(0)}{\alpha}\frac{d\bar{\alpha}(t)}{dt}. \tag{348}$$

Rearranging these terms yields

$$\left[1 - \frac{\tilde{K}(0)}{\alpha}\right]\frac{d\bar{\alpha}(t)}{dt} = -\tilde{K}(0)\bar{\alpha}(t), \tag{349}$$

or

$$\frac{d\bar{\alpha}(t)}{dt} = -\tilde{K}(0)\left[1 - \frac{\tilde{K}(0)}{\alpha}\right]^{-1}\bar{\alpha}(t). \tag{350}$$

This is the Markovian equation that we have sought. Thus by comparison with Eq. (325)

$$\tilde{K}(0)\left[1 - \frac{\tilde{K}(0)}{\alpha}\right] = K. \tag{351}$$

If Eq. (348) is iterated, the result is

$$\frac{d\bar{\alpha}(t)}{dt} = -\tilde{K}(0)\sum_{n=0}^{\infty}\frac{\tilde{K}^n(0)}{\alpha^n}\bar{\alpha}(t). \tag{352}$$

By comparison with Eq.

$$\sum_{n=0}^{\infty}\frac{\tilde{K}(0)^{n+1}}{\alpha^n} = K, \tag{353}$$

is obtained. We can simply illustrate Zwanzig's method for obtaining a Markovian equation from our non-Markovian equation (332) using the ansatz of Eq. (333). A parameter of slowness ξ is introduced such that

$$\left.\begin{aligned} s &= \xi x \\ t &= \tau/\xi \\ \bar{\alpha}(t) &= b(\tau) \end{aligned}\right\}, \tag{354}$$

when $\xi \to 0$, τ is kept fixed, and thus $t \to \infty$. In the Markovian equation

$$\frac{d\bar{\alpha}(t)}{dt} = -K\bar{\alpha}(t),$$

we notice that if K is made smaller the process becomes much slower. Thus, replacing K by ξK_m , and taking the limit $\xi \to 0$ is tantamount to making the process slow or to observing the long time behavior of the equation. Substituting our ansatz, Eq. (333), into Eq. (332) we have

$$\frac{d\bar{\alpha}(t)}{dt} = -\alpha K' \int_0^t dt_1 e^{-\alpha t_1} \bar{\alpha}(t-t_1). \tag{355}$$

Now from the Laplace convolution theorem (the Laplace transform $\tilde{\phi}(s)$ of the integral

$$\phi(t) = \int_0^t dt_1 f_1(t-t_1) f_2(t_1)$$

is the product of the Laplace transforms of the functions:

$$\tilde{\phi}(s) = \tilde{f}_1(s)\tilde{f}_2(s)$$

(see Eq. (334))), the Laplace transform of Eq. (355) is found to be

$$s\tilde{\alpha}(s) - \bar{\alpha}(0) = -\frac{\alpha K'}{\alpha + s}\tilde{\alpha}(s), \tag{356}$$

which when solved for $\tilde{\alpha}(s)$ yields

$$\tilde{\alpha}(s) = \frac{\bar{\alpha}(0)}{s + \frac{\alpha K'}{\alpha + s}}, \tag{357}$$

The inverse transform of Eq. (357) yields

$$\bar{\alpha}(t) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} ds\, e^{st} \frac{\bar{\alpha}(0)}{s + \frac{\alpha K'}{\alpha + s}} . \tag{358}$$

Introducing the parameter of slowness ξ, $K' = \xi K'_m$, and Eq. (358) becomes

$$b(\tau) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} d\chi\, e^{\chi\tau} \frac{\bar{\alpha}(0)}{\chi + \frac{\alpha K'_m}{\alpha + \xi\chi}} . \tag{359}$$

Taking the limit of Eq. (359) as $\xi \longrightarrow 0$ gives

$$\lim_{\xi\to 0} b(\tau) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} d\chi\, e^{\chi\tau} \frac{\bar{\alpha}(0)}{\chi + K'_m} . \tag{360}$$

There is a simple pole at $\chi = -K'_m$. Thus by using the residue theorem it is found that

$$\lim_{\xi \to 0} b(\tau) = e^{-K_m' \tau} \bar{\alpha}(0) \tag{361}$$

Now $\tau = \xi t$, $K_m' = \dfrac{K'}{\xi}$, and Eq. (361) becomes

$$\lim_{\xi \to 0} b(\tau) = e^{-K' t} \bar{\alpha}(0). \tag{362}$$

This is precisely the result one gets from the Markovian equations if K = K'. Thus in the limit $\xi \to 0$, the non-Markovian equation gives the correct Markovian limit. This completes our discussion of the general formulation of the non-Markovian regression of fluctuations.

3. The Momentum Autocorrelation Function

In this section the theory developed in the last section shall be applied to the problem of the momentum correlation function.

The transport equation for momentum relaxation is

$$\frac{d}{dt} \langle \underset{\sim}{P}_1(t) \rangle' = -\beta \langle \underset{\sim}{P}_1(t) \rangle'. \tag{363}$$

In this equation $\langle \underset{\sim}{P}_1(t) \rangle'$ is the average momentum of particle 1 at time t given that the initial momentum was $\underset{\sim}{P}_1(0)$, and β is the friction coefficient. Multiplying this equation by $\underset{\sim}{P}_1(0)$, and averaging over the equilibrium distribution of

$\underline{P}_1(0)$ yields

$$\frac{d}{dt}\langle \underline{P}_1(0)\cdot\underline{P}_1(t)\rangle = -\beta\langle \underline{P}_1(0)\underline{P}_1(t)\rangle. \tag{364}$$

$\langle \underline{P}_1(0)\cdot\underline{P}_1(t)\rangle$ is the momentum autocorrelation function. We may divide this equation by $\langle \underline{P}_1(0)^2\rangle$ which is $3mKT$, (from equipartition of energy) to normalize the correlation function. The normalized correlation function $\Psi(t)$ is therefore described by the following equation

$$\frac{d}{dt}\Psi(t) = -\beta\Psi(t), \tag{365}$$

with the boundary condition $\Psi(0) = 1$.

Equation (365) is a Markovian equation. The procedure outlined in the last section may be applied to this equation, if K is identified with β. The non-Markovian equation corresponding to Eq. (332) and (333) of the previous section is

$$\frac{d\Psi(t)}{dt} = -\int_0^t K(t_1)\,\Psi(t-t_1)\,dt_1. \tag{366}$$

The Laplace transform of this equation is found by using the convolution theorem,

$$s\tilde{\Psi}(s) - \Psi(0) = -\tilde{K}(s)\tilde{\Psi}(s), \tag{367}$$

with

$$\tilde{K}(s) = \frac{\alpha\gamma}{\alpha+s} . \tag{368}$$

If the procedure adopted in deriving Eq. (331) were used,

$$\gamma = \beta . \tag{369}$$

On the other hand, if Eq. (351) is used then

$$\gamma\left[1 + \frac{\gamma}{\alpha}\right]^{-1} = \beta . \tag{370}$$

There is yet a third relation for γ and α in terms of β. From Eq. (353) it is found that

$$\sum_{n=0}^{\infty} \frac{\gamma^{n+1}}{\alpha^{n}} = \beta . \tag{371}$$

Of course β is related to the diffusion coefficient through the Einstein relation,

$$\mathcal{D} = \frac{KT}{m\beta} . \tag{372}$$

Substituting Eq. (368) into Eq. (367) and solving for $\tilde{\Psi}(s)$ yields

$$\tilde{\Psi}(s) = \frac{1}{s+\tilde{K}(s)}\,\Psi(0), \tag{373}$$

$$= \frac{\alpha+s}{s^2+\alpha s+\alpha\gamma}\,\Psi(0),$$

$$\tilde{\Psi}(s) = \frac{\alpha+s}{(s-s_+)(s-s_-)}\,\Psi(0), \tag{374}$$

where

$$s_\pm = -\frac{\alpha}{2}\left[1 \mp \sqrt{1-4\gamma/\alpha}\,\right]. \tag{375}$$

The Laplace transform may be inverted to find $\Psi(t)$. $\tilde{\Psi}(s)$ has two first order poles at s_+ and s_-. Thus the residue theorem may be used to find the inverse transform

$$\Psi(t) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} ds\, e^{st}\,\frac{\alpha+s}{(s-s_+)(s-s_-)}, \tag{380}$$

$$\Psi(t) = \frac{\alpha + S_+}{S_+ - S_-} e^{S_+ t} - \frac{\alpha + S_-}{S_+ - S_-} e^{S_- t}. \tag{381}$$

It is easily verified that $\alpha + S_+ = -S_-$, and $\alpha + S_- = -S_+$. Equation (381) may therefore be written

$$\Psi(t) = \frac{1}{S_+ - S_-} \left\{ S_+ e^{S_- t} - S_- e^{S_+ t} \right\}. \tag{382}$$

In chapter I Eq. (13) a very useful relation was derived,

$$\frac{\partial^2}{\partial t^2} \langle \underline{P}_1(0) \cdot \underline{P}_1(t) \rangle = - \langle \underline{F}_1(0) \cdot \underline{F}_1(t) \rangle. \tag{383}$$

Since $\langle \underline{P}_1(0) \cdot \underline{P}_1(t) \rangle = 3mKT\ \Psi(t)$, Eq. (383) can be written in terms of the normalized momentum correlation function as

$$\langle \underline{F}_1(0) \cdot \underline{F}_1(t) \rangle = -3mKT \frac{\partial^2 \Psi(t)}{\partial t^2}. \tag{384}$$

Substituting Eq. (383) into (384) yields

$$\langle \underline{F}_1(0)\cdot\underline{F}_1(t)\rangle = -\frac{3mKT}{S_+-S_-}\left\{S_+S_-^2e^{S_-t}-S_-S_+^2e^{S_+t}\right\}. \tag{385}$$

In chapter I Eq. (23) a relation was derived which is also of interest.

$$\langle \underline{F}_1(0)\cdot\underline{F}_1(0)\rangle = KT\langle \nabla^2 V\rangle. \tag{386}$$

From Eq. (385) it is found that

$$\langle \underline{F}_1(0)\cdot\underline{F}_1(0)\rangle = 3mKT\,S_+S_- . \tag{387}$$

Combining Eqs. (386) and (387) yields

$$S_+S_- = \frac{\langle \nabla^2 V\rangle}{3m}. \tag{388}$$

From Eq. (375) it is found that $S_+S_- = \gamma\alpha$. In this way it is found that

$$\gamma\alpha = \frac{\langle \nabla^2 V\rangle}{3m}. \tag{389}$$

If Eq. (369) is used

$$\beta\alpha = \frac{\langle \nabla^2 V \rangle}{3m}, \tag{390}$$

a result which we shall have more to say about later. If Eq. (370) is used in conjunction with Eq. (389), γ , and α may be completely determined if $\langle \nabla^2 V \rangle$ and β can be found. As we shall see in section 6, β can be found from the measured diffusion coefficient, Eq. (372), and $\langle \nabla^2 V \rangle$ can be found from isotope separation data. In this way the velocity and force correlation function may be determined.

Equation (366) may be written

$$\frac{d\Psi(t)}{dt} = -\int_0^t K(t-t_1)\Psi(t_1)\,dt_1 \,. \tag{391}$$

If this equation is now differentiated with respect to t it is found that

$$\frac{d^2\Psi(t)}{dt^2} = -K(0)\Psi(t) - \int_0^t \frac{\partial K(t-t_1)}{\partial t}\Psi(t_1)\,dt_1 \,. \tag{392}$$

Of course Eq. (392) may be used to obtain Eq. (389) straightforwardly. Combining Eq. (386) and (384) gives

$$K(0) = \frac{\langle \nabla^2 V \rangle}{3m}, \tag{393}$$

$$K(0) = \alpha\gamma.$$

But it is not for this purpose that Eq. (392) was written. Substituting $K(t) = \alpha\gamma e^{-\alpha t}$ into Eq. (392) and performing the necessary integration yields the second order differential equation

$$\frac{d^2\Psi(t)}{dt^2} + \alpha\gamma\Psi(t) + \alpha\dot{\Psi}(t) = 0, \tag{394}$$

which becomes on substitution of Eq. (369),

$$\frac{d^2\Psi(t)}{dt^2} + \alpha\beta\Psi(t) + \alpha\dot{\Psi}(t) = 0. \tag{395}$$

Equation (395) is interesting for reasons that will be made clear in section 7.

4. The Power Spectrum of the Velocity, the Mean Square Displacement of a Particle, the First and Second Order Moments of the Momentum

We have already discussed the autocorrelation function of a random variable; such as the momentum of a particle. We have made the tacit assumption that the momentum of a particle is a stationary random process, which means that the autocorrelation function is independent of the origin of time. If $\underline{\alpha}(t)$ is a random variable, then stationarity may be summarized as follows,

$$\phi(\tau) = \langle \underline{\alpha}(t) \cdot \underline{\alpha}(t+\tau) \rangle. \tag{396}$$

That is ϕ is a function of τ and not of t. The Fourier transform of $\bar{\underline{\alpha}}(t)$ may be taken as

$$\underline{\alpha}(\omega) = \int_{-\infty}^{+\infty} \bar{\underline{\alpha}}(t)\, e^{i\omega t} dt, \tag{397}$$

the inverse transform as

$$\underline{\alpha}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \underline{\alpha}(\omega)\; e^{-i\omega t} d\omega. \tag{398}$$

Inserting this last relation into Eq. (396) yields

$$\phi(\tau) = \frac{1}{4\pi^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \langle \underline{\alpha}(\omega) \cdot \underline{\alpha}(\omega') \rangle \cdot e^{-i\omega t - i\omega'(t+\tau)} d\omega d\omega'. \tag{399}$$

Equation (396) requires that the right-hand side of this equation be independent of t. To insure that Eq. (396) is satisfied the condition

$$\langle \underline{\alpha}(\omega)\cdot\underline{\alpha}(\omega')\rangle = \langle \alpha^2(\omega)\rangle\,\delta(\omega+\omega') \tag{400}$$

is imposed. Although $\underline{\alpha}(\omega)$ is complex, $\langle \alpha^2(\omega)\rangle$ is evidently real. The quantity $\langle \underline{\alpha}(\omega)\underline{\alpha}(\omega')\rangle$ differs from zero only when $\omega' = -\omega$, thus the quantity $\langle \alpha^2(\omega)\rangle = \langle \alpha^*(\omega)\cdot\alpha(\omega)\rangle$ which is real. Inserting Eq. (400) into (399) and performing the ω' integration yields

$$\phi(\tau) = \frac{1}{4\pi^2}\int_{-\infty}^{+\infty}\langle \alpha^2(\omega)\rangle e^{-i\omega\tau}\,d\omega. \tag{401}$$

From Eq. (366) we find that

$$\phi(0) = \langle \alpha(0)^2\rangle = \frac{1}{4\pi^2}\int_{-\infty}^{+\infty}\langle \alpha^2(\omega)\rangle\,d\omega. \tag{402}$$

By analogy with electrical systems where $\underline{\alpha}(t)$ is the current at time t, and $\langle \alpha^2\rangle$ is the power $\langle \alpha^2(\omega)\rangle$ may be viewed as a generalized power spectrum. Since $\langle \alpha^2(\omega)\rangle = \langle \underline{\alpha}(\omega)\cdot\underline{\alpha}(-\omega)\rangle$ the integrand in Eq. (402) is even and we may therefore write it as

$$\phi(0) = \frac{2}{4\pi^2}\int_0^{\infty} \langle \alpha^2(\omega) \rangle d\omega \, . \tag{403}$$

We therefore call $\langle \alpha^2(\omega) \rangle / 2\pi$ the power spectrum associated with the random variable $\underset{\sim}{\alpha}(t)$. The following notation shall be used

$$G(\omega) = \frac{1}{2\pi} \langle \alpha^2(\omega) \rangle , \tag{404}$$

and Eq. (401) becomes

$$\begin{aligned} \phi(\tau) &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} \frac{\langle \alpha^2(\omega) \rangle}{2\pi} e^{-i\omega\tau} d\omega , \\ &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} G(\omega) e^{-i\omega\tau} d\omega . \end{aligned} \tag{405}$$

Equation (405) may be inverted to give

$$G(\omega) = \int_{-\infty}^{+\infty} \phi(\tau) e^{i\omega\tau} d\tau \, . \tag{406}$$

To obtain a result expressed only in terms of future times, i.e. for $\tau > 0$, we may split the region of integration $(-\infty, 0)$, $(0, \infty)$ and make use of the stationarity condition.

$$\langle \underline{\alpha}(\tau)\cdot\underline{\alpha}(0)\rangle = \langle \underline{\alpha}(0)\cdot\underline{\alpha}(-\tau)\rangle, \tag{407}$$

to obtain

$$G(\omega) = G_+(\omega) + G_-(\omega), \tag{408}$$

where

$$\begin{aligned} G_+(\omega) &= \int_0^\infty e^{i\omega\tau}\phi(\tau)\,d\tau, \\ G_-(\omega) &= \int_0^\infty e^{-i\omega\tau}\phi(\tau)\,d\tau. \end{aligned} \tag{409}$$

At this point it may be noted that

$$G_+(\omega) = G_-(-\omega), \tag{410}$$

and

$$\begin{aligned} G(\omega) &= 2\int_0^\infty \phi(\tau)\left\{\frac{e^{i\omega\tau}+e^{-i\omega\tau}}{2}\right\}d\tau \\ &= 2\int_0^\infty \phi(\tau)\cos\omega\tau\,d\tau. \end{aligned} \tag{411}$$

Thus $G(\omega)$ as we have defined it may be expressed as the cosine transform of the autocorrelation function. This is the famous Wiener-Khinchine Theorem.

The power spectrum $G_p(\omega)$ associated with the normalized velocity correlation function defined in the last section may be defined from Eq. (411) as

$$G_p(\omega) = 2\int_0^\infty \Psi(\tau)\cos\omega\tau\, d\tau. \tag{412}$$

For convenience in comparing these results with future work, we define a function $f(\omega) = \frac{\gamma}{2} G_p(\omega)$,

$$f(\omega) = \gamma\int_0^\infty \Psi(\tau)\cos\omega\tau\, d\tau. \tag{413}$$

Substituting Eq. (382) into Eq. (413) and integrating yields

$$f(\omega) = -\frac{S_+S_-(S_- + S_+)\gamma}{(S_+^2+\omega^2)(S_-^2+\omega^2)}, \tag{414}$$

or in terms of α, β, γ, ω,

$$f(\omega) = \frac{\alpha^2\gamma^2}{\alpha^2\gamma^2 + \alpha^2(1-2\gamma/\alpha)\omega^2 + \omega^4}. \tag{415}$$

Another quantity that we want to find is the mean square displacement of a molecule as a function of time.

$$\underset{\sim}{\Delta R_1}(t) = \int_0^t \underset{\sim}{v_1}(t_1)dt_1. \tag{416}$$

Thus

$$\langle \underset{\sim}{\Delta R_1}(t)\cdot \underset{\sim}{\Delta R_1}(t)\rangle = \langle \underset{\sim}{\Delta R_1}(t)^2\rangle,$$

$$\langle \underset{\sim}{\Delta R_1}(t)^2\rangle = \int_0^t\int_0^t \langle \underset{\sim}{v_1}(t_1)\cdot\underset{\sim}{v_1}(t_2)\rangle dt_1\, dt_2, \tag{417}$$

$$= \frac{1}{m^2}\int_0^t\int_0^t \langle \underset{\sim}{P_1}(t_1)\cdot \underset{\sim}{P_1}(t_2)\rangle dt_1 dt_2 . \tag{418}$$

Because $\underset{\sim}{P_1}(t)$ is assumed to be a stationary random variable, $\langle \underset{\sim}{P_1}(t_1)\cdot \underset{\sim}{P_1}(t_2)\rangle = \langle \underset{\sim}{P_1}(0)\cdot \underset{\sim}{P_1}(t_2-t_1)\rangle$. Substituting this into Eq. (418) and using the definition of the normalized momentum correlation function, it is found that

$$\langle \Delta R_1(t)^2\rangle = \frac{3KT}{m}\int_0^t\int_0^t dt_1 dt_2 \Psi(t_2-t_1). \tag{419}$$

Transforming the variables to $\tau = t_2 - t_1$, and $T = t_1 + t_2$ where

$$\left| \frac{\partial(t_1, t_2)}{\partial(\tau, T)} \right| = \frac{1}{2},$$

and the limits of integration are $T = (0, 2t)$ and $\tau = (-t, t)$ yields

$$\langle \Delta R_1^2(t) \rangle = \frac{3KT}{2m} \int_0^{2t} dT \int_{-t}^{t} d\tau \, \Psi(\tau). \tag{420}$$

To check this formula we apply it to the well known case of Brownian motion where $\Psi(\tau) = e^{-\beta\tau}$. The result is the same as that found by Chandrasekhar.

Furthermore, Eq. (420) may be used in yet another way. Eq. (420) may be written as

$$\langle \Delta R_1(t)^2 \rangle = \frac{6KT}{m} t \int_0^{t} d\tau \, \Psi(\tau). \tag{421}$$

The definition of the diffusion coefficient is

$$\mathcal{D} = \lim_{t \to \infty} \frac{\langle \Delta R_1(t)^2 \rangle}{6t}. \tag{422}$$

When Eq. (421) is substituted into Eq. (422), and the fact that Ψ is an even function of τ is exploited,

$$\mathcal{D} = \lim_{t \to \infty} \frac{\langle \Delta R_1^2(t) \rangle}{6\, t} = \frac{KT}{m} \int_0^\infty d\tau\, \Psi(\tau) \tag{423}$$

is obtained. Eq. (381) may now be used and the integral in Eq. (423) evaluated yielding

$$\mathcal{D} = -\frac{KT}{m} \frac{(S_- + S_+)}{S_+ S_-} . \tag{424}$$

Eq. (375) may be used to find,

$$\mathcal{D} = \frac{KT}{m\gamma} ,$$

which, if $\gamma = \beta$, is precisely the Einstein relation Eq. (372). This result strongly indicates that Eq. (369) is the one that should be used for computational pruposes. This was also suggested by Eq. (362).

For reasons that will become clear in the discussion, the time dependence of the following moments will be needed.

$$\langle \Delta \underline{P}_1(t) \rangle' = \langle \underline{P}_1(t) \rangle' - \underset{\sim}{P_1}(0) \tag{425}$$

and

$$\langle (\Delta \underset{\sim}{p}_1^2(t)) \rangle = \langle \underset{\sim}{p}_1(t)^2 \rangle' - \underset{\sim}{p}_1^2(0). \tag{426}$$

The subscript 1 indicates that the average is performed in an ensemble in which the initial momentum of particle 1 is fixed. The first moment is simply found to be

$$\langle \Delta \underset{\sim}{p}_1(t) \rangle' = \left[\Psi(t) - 1 \right] \underset{\sim}{p}_1(0). \tag{427}$$

The second moment is a bit more difficult to find. Remembering that

$$\Delta \underset{\sim}{p}_1(t) \equiv \int_0^t \underset{\sim}{F}_1(t_1)\, dt_1 , \tag{428}$$

where $\underset{\sim}{F}_1$ is the force acting on particle 1, the second moment is found to be

$$\langle (\Delta \underset{\sim}{p}_1(t))^2 \rangle = \int_0^t \int_0^t \langle \underset{\sim}{F}_1(t_1) \cdot \underset{\sim}{F}_1(t_2) \rangle\, dt_1\, dt_2 . \tag{429}$$

Remembering that the force is assumed to be a stationary random variable, and performing the same change of variable as in obtaining Eq. (420), it is found that

$$\langle (\Delta \underline{P}_1(t))^2 \rangle = \frac{1}{2} \int_0^{2t} dT \int_{-t}^{+t} d\tau \langle \underline{F}_1(0) \cdot \underline{F}_1(\tau) \rangle . \tag{430}$$

Equation (384) may now be used in Eq. (430) to obtain

$$\langle (\Delta P_1(t))^2 \rangle = - \frac{3mKT}{2} \int_0^{2t} dT \int_{-t}^{t} \frac{\partial^2 \psi(\tau)}{\partial \tau^2} d\tau . \tag{431}$$

Here it is assumed that $\frac{\partial^2 \psi}{\partial \tau^2}$ is an even function of τ.

$$\begin{aligned} \langle (\Delta \underline{P}_1(t))^2 \rangle &= -6mKTt \int_0^{t} \frac{\partial^2 \psi(\tau)}{\partial \tau^2} d\tau \\ &= -6mKTt \frac{\partial \psi(t)}{\partial t} . \end{aligned} \tag{432}$$

Equations (428) and (432) are the desired results.

5. Relaxation Time Equation

In this section a very simple kinetic model shall be discussed. It should be pointed out immediately that this model is studied for heuristic reasons only. It is indeed much less meaningful than all the work discussed in the previous sections, but it serves to clarify some points because it begins with a kinetic equation. The work presented here is closely related to work done by Haubold[73] and by Van Hove and Verboven.[74,75]

It is assumed that the following kinetic equation describes the time evolution of the single particle velocity distribution function $\varphi_1(v_1, t)$ for a homogeneous system in the Markovian approximation

$$\frac{\partial \varphi}{\partial t}(v_1, t) = -\gamma \left[\varphi(v_1, t) - \varphi^{(0)}(v_1) \right]. \tag{433}$$

Here $1/\gamma$ is a relaxation time, and $\varphi^{(0)}(v_1)$ is the equilibrium velocity distribution function which is Maxwellian. Defining $\delta\varphi(v_1, t) = \varphi(v_1, t) - \varphi^{(0)}(v_1)$ as the deviation of the distribution function from equilibrium Eq. (433) may be written

$$\frac{\partial \delta\varphi(v_1, t)}{\partial t} = -\gamma\, \delta\varphi(v_1, t). \tag{434}$$

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73. K. Haubold, Physica 28, 834 (1962).

74. L. Van Hove, and E. Verboven, Physica 27, 418 (1961).

75. E. Verboven, J. Math. Phys. 4, 266 (1963).

We want to find the non-Markovian kinetic equation which reduces to Eq. (434) in the Markovian limit, i.e., for long times.

It will be remembered that Prigogine and co-workers have derived the following master equation for the velocity distribution in a homogeneous system

$$\frac{\partial \delta \varphi(v_1,t)}{\partial t} = -\int_0^t dt_1\, G(t-t_1)\,\delta\varphi(t_1) + F^+(t_1), \tag{435}$$

where $F^+(t_1)$ is a destruction fragment representing the finite range of the initial spatial correlations. It is assumed that $F^+(t_1)$ damps out very quickly. The remaining term on the right-hand side of Eq. (435) describes the scattering process or collision process which makes $\varphi(v_1,t)$ evolve towards equilibrium. The equation, as it stands, is non-Markovian because $\delta\varphi(v_1,t)$ depends on an integration over its whole history. As before, we want to choose $G(t-t_1)$ in such a way that Eq. (435) reduces to Eq. (434) for long times. We adopt the "ansatz" as before that

$$G(t-t_1) = \mu\gamma\, e^{-\mu(t-t_1)}. \tag{436}$$

Substituting Eq. (436) into Eq. (435), multiplying the resulting equation by $\underset{\sim}{v_1}$ and integrating over d^3v_1, it is found that

$$\frac{\partial}{\partial t} \langle \underset{\sim}{v}_1(t) \rangle = -\mu\nu \int_0^t e^{-\mu(t-t_1)} \langle \underset{\sim}{v}_1(t_1) \rangle \, dt_1 \tag{437}$$

where

$$\langle v_1(t) \rangle = \iiint \delta\varphi(v_1, t)\, \underset{\sim}{v}_1 \, d^3 v_1$$

$$= \iiint \varphi(v_1, t)\, \underset{\sim}{v}_1 \, d^3 v_1 \tag{438}$$

because the equilibrium average is zero.

Actually what is wanted is the average value of $\underset{\sim}{v}_1(t)$ given that at time zero the velocity was $\underset{\sim}{v}_1(0)$. This can be stated in terms of a boundary condition on Eq. (435).

$$\delta\varphi(v_1, 0) = \delta(\underset{\sim}{v}_1 - \underset{\sim}{v}_1(0)) - \varphi^{(0)}(v_1) . \tag{439}$$

Thus

$$\langle \underset{\sim}{v}_1(0) \rangle = \iiint \delta(\underset{\sim}{v}_1 - \underset{\sim}{v}_1(0))\, \underset{\sim}{v}_1 \, d^3 v_1 \tag{440}$$

$$= \underset{\sim}{v}_1(0) ,$$

given this initial condition, Eq. (437) becomes

$$\frac{d}{dt}\langle \underset{\sim}{v}_1(t)\rangle' = -\mu\nu\int_0^t e^{-\mu(t-t_1)}\langle \underset{\sim}{v}_1(t_1)\rangle' dt_1 \tag{441}$$

where the 1 indicates a fixed ensemble average in accordance with Eq. (439). Multiplying Eq. (441) by $\underset{\sim}{v}_1(0)$, and averaging this over the Maxwellian distribution then gives, after diving by $\langle \underset{\sim}{v}_1(0)^2\rangle$,

$$\frac{d\psi(t)}{dt} = -\mu\nu\int_0^t e^{-\mu(t-t_1)}\psi(t_1)dt_1, \tag{442}$$

which is of the same form as Eq. (366). The procedure discussed in the preceeding sections may now be applied to Eq. (442) and identical results are obtained.

It must be emphasized that this derivation of Eq. (442) is inferior to the previous derivation if for no other reason that the relaxation time equation is unworthy of the slightest recognition. It corresponds to no known physical system. Furthermore, the regression of fluctuations in the Markovian limit is adequately described by a relaxation time equation of the form of Eq. (325); whereas, the distribution function is scarcely if ever represented by a relaxation equation. The procedure followed here could have been used for the Fokker-Planck equation. Some recent work by Brocas[76] contains the relevant information.

6. Numerical Calculations

The computer experiment of Rahman was performed at $94.4^{o}K$ and a density of 1.374 g/cm^{-3}. The calculations based upon the work presented here were done for the same conditions. Several calculations of the normalized momentum correlation function, and the corresponding power spectrum were performed. In addition the mean square displacement, and the second moment of the momentum as a function of time were calculated. All of these calculations are displayed in Figs. (1)--(24), which occupy the following pages. The reason that many calculations were performed is simple: uncertainty in data. As was shown in the preceeding pages a knowledge of the diffusion coefficient, and of the mean square force, or the mean Laplacian of the potential, is sufficient for the determination of the parameters α and γ through Eqs. (369), (370), and (371). The difficulty arises from the fact that the computer calculations of Rahman yield a diffusion coefficient D = $2.4 \times 10^{-5} \frac{cm^2}{sec}$ whereas the value measured by Nagigadeh and Rice[77] is $D = 2.72 \times 10^{-5} \frac{cm^2}{sec}$. The difference between the computer results and the experiment may be explained by the fact that Rahman used a Lennard-Jones potential with parameters

76. J. Brocas, private communication.

77. J. Nagigadeh and S. A. Rice, J. Chem. Phys. 36, 2710 (1962).

obtained from gas phase measurements. If the intermolecular forces are adequately represented by a Lennard-Jones potential it is almost certain that the parameters will not be the same as those measured in the gas phase. Furthermore, it is not at all certain that the intermolecular potential is a Lennard-Jones potential. Certainly there must be three body effects present to change the picture even more. In point of fact, Rahman has made the calculation of the diffusion coefficient for the same fluid except with a modified Buckingham potential and reports better agreement with the measurements of Nagizadeh and Rice. Thus one should use the diffusion coefficient calculated by Rahman instead of the experimental value, for the real value does not correspond to the argon model used by Rahman. The procedure adopted here was to perform the calculation for both values of the diffusion coefficient so that both sides of the argument are adequately presented.

A similar difficulty arises when the term $\langle \nabla^2 V \rangle$ is considered. As was mentioned in Chapter II this quantity can be obtained from isotope separation data for argon liquid in equilibrium with argon vapor at the temperature and density stated above. The data are scanty, and the inaccuracies in choosing the correct value are large. The data are presented in Fig. (24) for the benefit of the reader. Furthermore, this data corresponds to the real intermolecular potential whereas Rahman is dealing with a highly idealized potential. For the same reasons as stated in the case of the diffusion coefficient it is felt that it would be better to use a value for $\langle \nabla^2 V \rangle$

computed by Rahman, had he performed this calculation. Unfortunately, he did not; there is, however, a way to find it from his data.

The right-hand side of Eq. (366) may be Taylor expanded and only the term linear in t retained,

$$\begin{aligned}\frac{d\Psi(t)}{dt} &= -\left[K(t)\Psi(0) + \int_0^t K(t_1)\frac{d\Psi(t-t_1)}{dt}dt_1\right]_{t=0} t + \cdots \\ &= -K(0)\Psi(0)t + \cdot \\ &= -\alpha\gamma t .\end{aligned} \tag{443}$$

Thus for $t \to 0$ if we measure the slope in Rahman's computed correlation function we may find $\alpha\gamma$, and thereby perform the remaining calculations. When this is done $\langle\nabla^2 V\rangle$ is found to be 11.0 x 10^3 ergs/cm^2 as compared to 10.7 x 10^3 ergs measured by Boata.

We present here a sample calculation of the velocity correlation function and its power spectrum for argon at T = 94.4°K and ρ = 1.374 g/cc. Rahman's value of the diffusion coefficient D = 2.43 x 10^{-5} $\frac{cm^2}{sec}$ is used. The best value for $\langle\nabla^2 V\rangle$ that can be picked from Rahman's calculation appears to be 11.0 x 10^3 $\frac{erg}{cm^2}$. For this sample calculation we take γ = β as given in Eq. (369). Actually Eq. (370) or Eq. (371), should be used but the numerical work is a bit more complicated. Eqs. (369) and (371) are used, and the results are displayed in the following curves; however, for the sake of the sample calculation Eq. (369) is chosen.

Equation (45) is used to find β,

$$\beta = \frac{KT}{m\mathcal{D}} = 8.06 \times 10^{12}\ sec^{-1}. \tag{444}$$

Equation (390) is used to obtain αβ,

$$\alpha\beta = \frac{<\nabla^2 V>}{3m} = 0.65 \times 10^{26}\ sec^{-2}. \tag{445}$$

From Eqs. (444) and (445) α is found to be

$$\alpha = 8.06 \times 10^{12}\ sec^{-1}, \tag{446}$$

and

$$\beta/\alpha = 1.0. \tag{447}$$

Now

$$b^2 = 1 - 4\,\beta/\alpha = -3.0\ . \tag{448}$$

Thus we see from Eq. (375) that $S_\pm$ is complex. When this is substituted into Eq. (388) it is found that

$$\Psi(\tau) = e^{-4.02\tau}\left[\cos(7.03\tau) + 0.33\sin(7.03\tau)\right].$$

It should be noted that this function shows damped oscillatory behavior. $\Psi(\tau)$ will always have oscillations if $b^2 < 0$ however, in the case that $b^2 \geq 0$ there are no oscillations in $\Psi(\tau)$. This effect is seen to be density dependent because $\alpha\beta$ is related to the mean square force which is density dependent.

Using the values for α and β in Eq. (415) yields

$$f(\omega) = \frac{0.420}{0.420 - .65\times 10^{-26}\omega^2 + 10^{-52}\omega^4}. \tag{449}$$

Eq. (421) may be used to compute the mean square displacement. It is convenient to present this function in a different form. A function T(t) may be defined

$$T(t) = \frac{\langle \Delta R_1^2(t)\rangle}{6\mathcal{D}} = \frac{KT}{m\mathcal{D}}\, t\int_0^t d\tau\, \Psi(\tau), \tag{450}$$

$$= \beta t\int_0^t d\tau\, \Psi(\tau). \tag{451}$$

When α and β as computed in Eqs. (444) and (446), are used

$$T(\tau) = e^{-4.03\tau}\left[-\cos(6.86\tau) + 0.557\sin(6.86\tau)\right] + \tau.$$

Eq. (432) may be used to compute the 2nd moment of the momentum. Again it is convenient to present this function in a different form. A function P(t) may be defined as

$$P(t) = \frac{\langle(\Delta P_1(t))^2\rangle}{6mKT} = -t\,\frac{d\Psi(t)}{dt}. \tag{452}$$

Again, when α and β are computed from Eqs. (444) and (446) are used

$$P(\tau) = -\left[9.52\,e^{-4.03\tau}\sin(6.86\tau)\right]\tau.$$

The following curves are all explicitly labelled so that they will be immediately identifiable. Rahman's calculations are also presented, and the qualitative agreement is obvious.

7. Discussion

The normalized momentum correlation function and its associated power spectrum calculated on the basis of the theory presented in this chapter reproduce the computer calculations fairly well. The positions of the maxima and minima of these functions are in very good agreement with the computer calculations of Rahman. There are some differences however. In the region $.65 < \tau < 1.3$, Rahman's autocorrelation function remains negative whereas the function calculated by theory becomes positive. Furthermore, Rahman's power spectrum shows oscillatory behavior after the first peak whereas the function calculated by theory does not.

Needless to say, the agreement is far better than one might have expected for such a simple theory. The simplest non-Markovian kernel was chosen as an ansatz. Certainly no Markovian equation could account for the oscillations.

The motion of a particle may be interpreted in the following manner. In a dense medium a particle is trapped in a cage made up of its nearest neighbors. This particle moves within the cage bouncing from wall to wall and thereby executing a quasi-oscillatory motion. While the particle is in the cage, before its momentum has decayed to the thermal average, the cage changes shape and thereby effects the motion of the molecule. In this way the configuration of the fluid effects the momentum decay of the particle. The correlation time of the cage, that is the time necessary for the cage to loose order, therefore enters the momentum correlation function in a natural way. It is very likely that the configurational correlation, or relaxation time is $1/\alpha$.

Although the last statement cannot be proved, a plausibility argument may be developed. Equation (395) was found assuming that $\gamma = \beta$. It just happens that this very same differential equation for the momentum correlation function was derived by Gray on entirely different grounds. Gray hypothesized a relaxation equation for the pair correlation function and thereby found Eq. (395). The parameter α which appears in Eq. (395) corresponds to $1/\tau_c$ in his theory, where τ_c is the configurational relaxation time.

It must be pointed out here that Gray's model rests on a model kinetic equation for the evolution of the pair correlation function, which is physically appealing, but is restrictive because it pins down the statistical behavior of the system. The procedure adopted in this work rests on a particularly simple ansatz, and is not restrictive because the non-Markovian equation found may be consistent with many kinetic equations, as indeed it is. It is consistent with the two equations already discussed, the relaxation time equation presented here, and Gray's equation. Furthermore, it is consistent with the non-Markovian equations which reduce to the Fokker-Planck equation and the Crook equation, if a similar ansatz is chosen.

There is one further point that must be made. To derive a Fokker-Planck equation there must exist a time such that

$$\tau_F << \tau < \tau_P ,$$

and for which

$$\langle \Delta \underline{P}_1(\tau) \rangle' \sim \tau ,$$
$$\langle (\Delta \underline{P}_1(\tau))^2 \rangle' \sim \tau ,$$

and all higher moments $\sim \tau^n$, $n > 1$. Equations (428) and (479) may be used to see whether this is true or not. Equation (382) may be expanded about t = 0 to give

$$\Psi(\tau) = 1 - S_+ S_- \tau^2 .$$

From Eq. (48) and (43) it is found that

$$S_+ S_- = \alpha \gamma .$$

Thus

$$\Psi(\tau) = 1 - \alpha \gamma \tau^2 ;$$

and

$$\langle (\Delta \underline{P}_1(\tau)) \rangle' = - \alpha \beta \tau^2 .$$

From Eq. (432) it is also seen that

$$\langle (\Delta \underline{P}_1(\tau))^2 \rangle' = 2mKT \tau^2$$

for small τ. This should be expected since for short times a particle behaves coherently; that is, for short times a particles position and momentum may be predicted from its initial conditions through the classical equations of motion. In Figs. (11)--(22) we see that $\Psi(t)$ and consequently $\langle \Delta p_1(\tau)\rangle'$, and $\langle \Delta p_1^2(\tau)\rangle'$ become linear in τ for

$$0.3 < \tau .$$

If it is remembered that $\tau_p = 1/\beta \times 10^{-12} = 0.124$, it can be seen that the necessary condition for the Fokker-Planck equation is not met; that is the first and second moments of the momentum only become linear for times greater than the momentum correlation time. Of course when the Fokker-Planck equation is derived, a Markov process is assumed. The Markovian correlation function is used to calculate the moments of the momentum. We see here, however, that for short time behavior this cannot be done. For short times non-Markovian effects are important. These statements may be made on the basis of Rahman's computer experiment.

There is another very interesting feature of Eq. (390). Since $\beta = \frac{1}{m}\zeta^{(1)}$, equation (390) becomes

$$\alpha \zeta^{(1)} = \frac{\langle \nabla^2 V \rangle}{3}$$

Thus if $\alpha = 2\zeta^{(2)}/m$ we retrieve Eq. (166) of Chapter II that is

$$\zeta^{(2)}\zeta^{(1)} = \frac{m}{6}\langle \nabla^2 V \rangle .$$

This is very interesting because, Gray also finds Eq. (390). These three independent derivations of equations like Eq. (390) are amazing. $\zeta^{(2)}$ it will be remembered, was related to $\langle \Delta \underline{R}_{12}(\tau) \Delta \underline{R}_{12}(\tau) \rangle^{1/2}$ which measures the diffusion of one particle in the presence of another; and is therefore, in some rather vague way connected with the configurational memory or configurational relaxation time.

Rahman computed the pair correlation function for argon. This computed function may be considered exact for the model system. One possible way to see whether or not the model system corresponds to real liquid argon is to use the model pair correlation function in conjunction with the equation of state and the energy equation to predict the pressure and heat of vaporization. Rahman was kind enough to make his data available to us for this test. A Simpson's rule integration was carried out and the pressure obtained was 51.2 atm. The energy of vaporization obtained was 1335 $\frac{\text{cal}}{\text{mole}}$. The measured pressure of liquid argon at 94.4°K and 1.374 gm/cm^3 is around 160 atm, and the energy of vaporization is around 1550 $\frac{\text{cal}}{\text{mole}}$. The agreement is fairly good, especially when it is remembered that the pressure is a very sensitive test of an equilibrium pair correlation function. Most theories of the pair correlation function give much worse agreement than this. It may nevertheless be concluded that the Lennard-Jones potential does not adequately represent the molecular interactions in a dense fluid such as argon.

Fig. 1.--The momentum autocorrelation function $\Psi(\tau)$ versus τ ($t \times 10^{12}$), from Rahman's computer experiment.

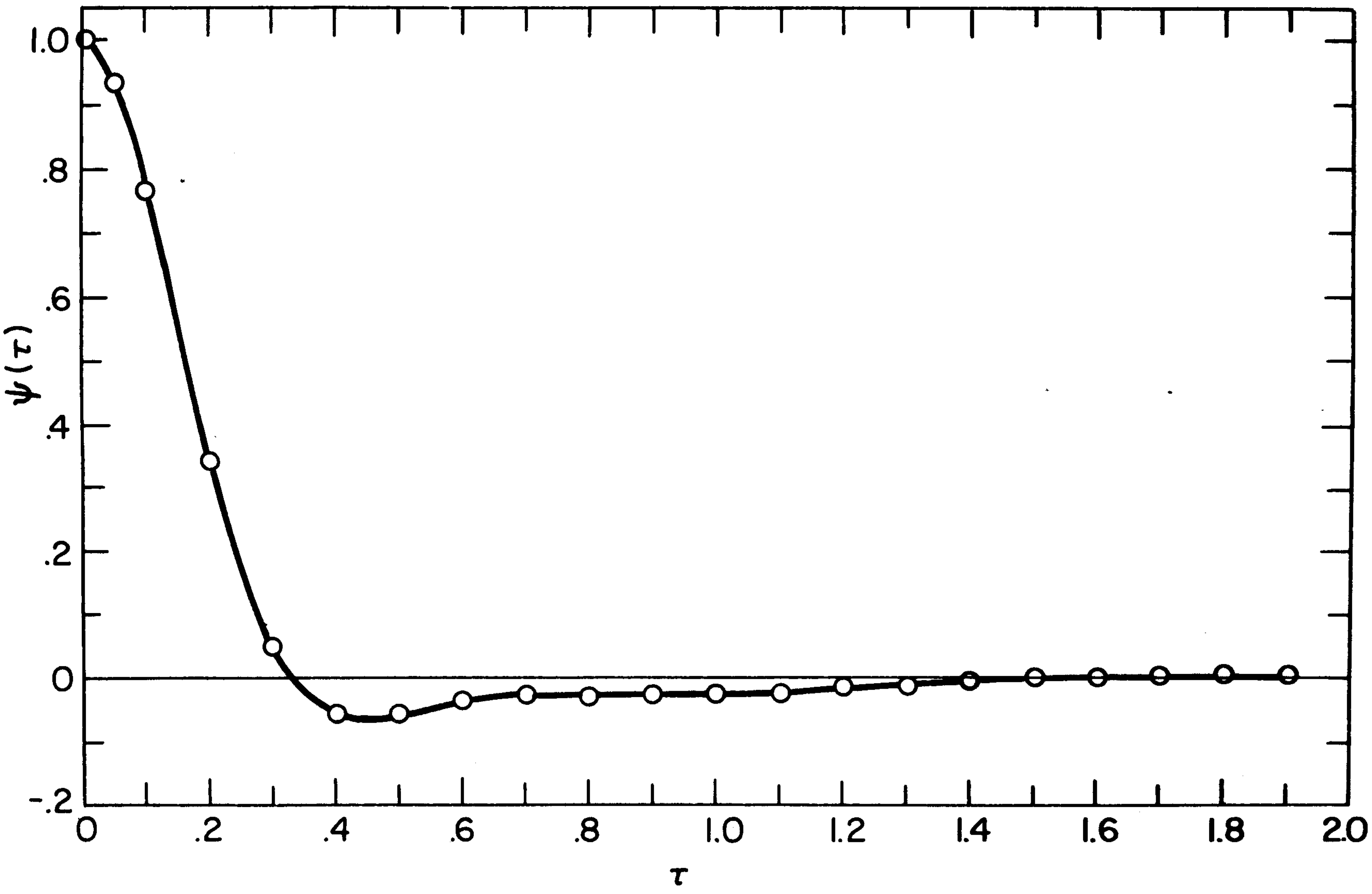

1.0
.8
.6
.4
.2
0
-.2
ψ(τ)
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 2.--The momentum autocorrelation function $\psi(\tau)$ versus τ $(t \times 10^{12})$, in the Markovian approximation.

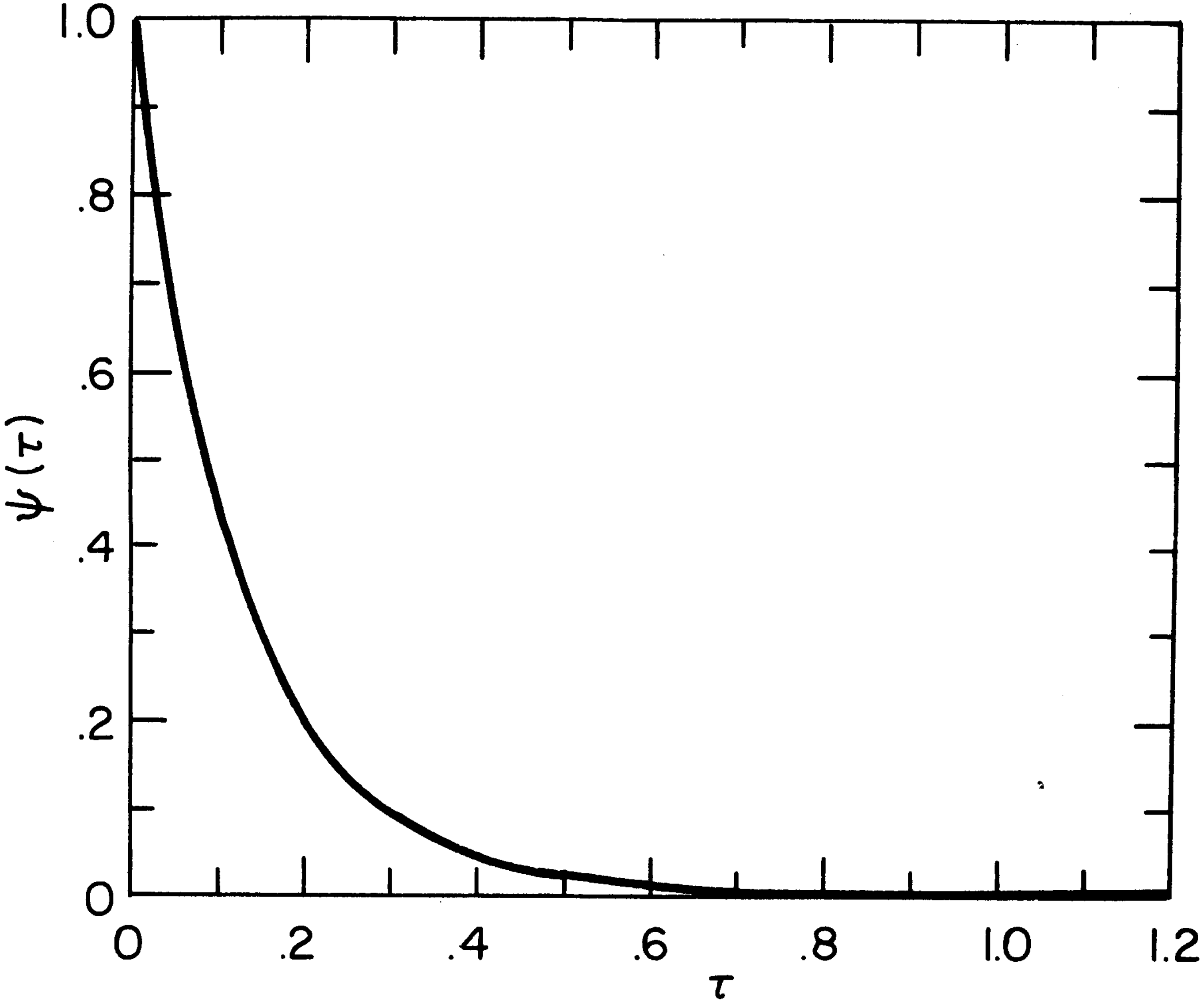
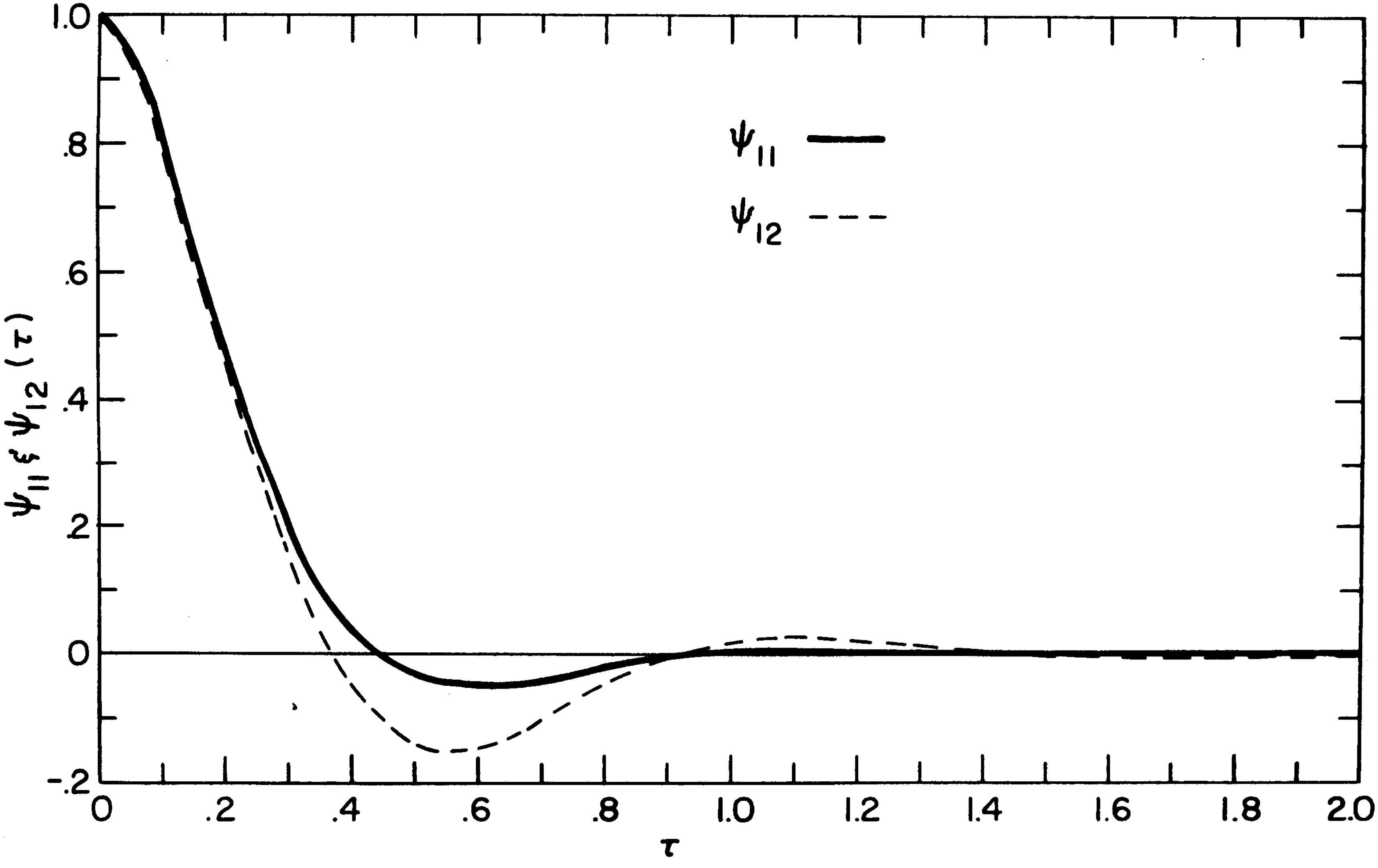
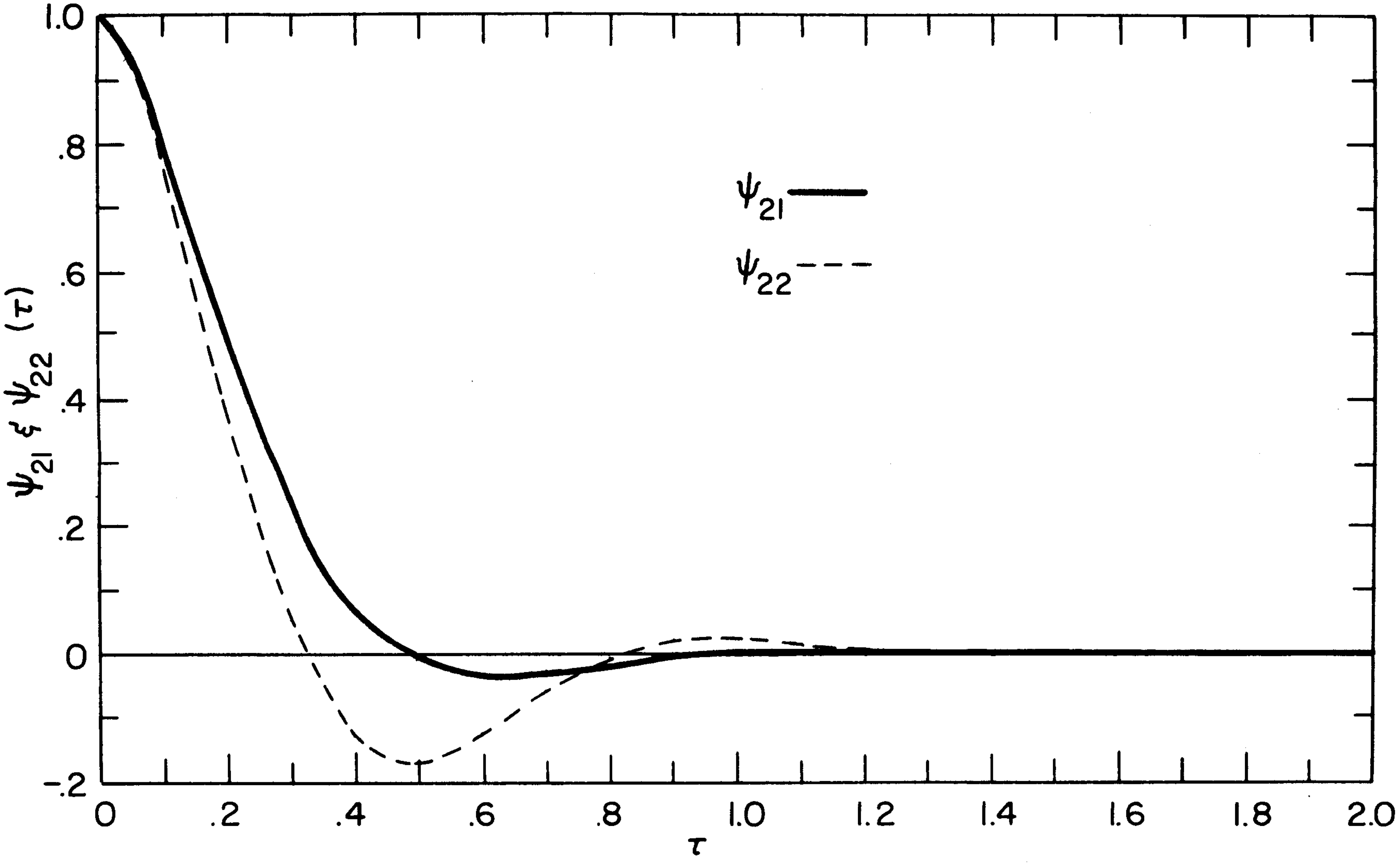

1.0
.8
.6
.4
.2
0
ψ (τ)
0
.2
.4
.6
.8
1.0
1.2
τ

Fig. 3.--The momentum autocorrelation functions $\Psi_{11}(\tau)$ and $\Psi_{12}(\tau)$, versus τ (t x 10^{12}), from Eq. (371) (solid line), and Eq. (369) (dashed line) respectively for D = 2.43 x 10^{-5} cm^2/sec and $\langle \nabla^2 V \rangle = 10.7 \times 10^3 \frac{\text{ergs}}{\text{cm}^2}$.



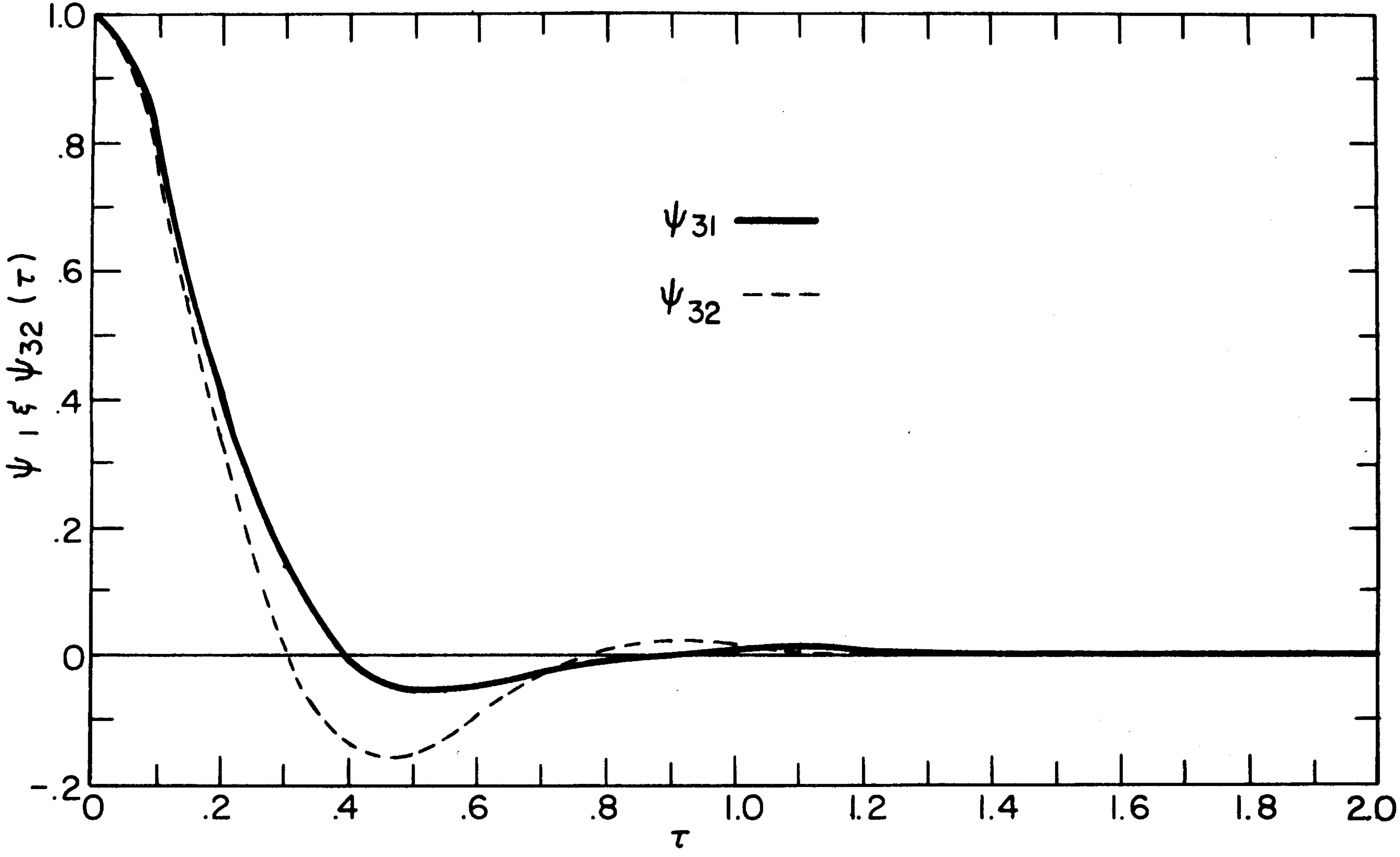
1.0
.8
.6
.4
.2
0
-.2
ψ_{11} ξ ψ_{12} (τ)
ψ_{11}
ψ_{12}
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 4.--The momentum autocorrelation functions $\Psi_{21}(\tau)$ (solid line) and $\Psi_{22}(\tau)$ (dashed line) versus τ (t x 10^{12}) from Eqs. (371) and (369) respectively, for D = 2.72 x 10^{-5} cm^2/sec and $\langle \nabla^2 V \rangle = 10.7 \times 10^3 \, \frac{\text{ergs}}{\text{cm}^2}$.



1.0
.8
.6
.4
.2
0
-.2
ψ_{21} ξ ψ_{22} (τ)
ψ_{21}
ψ_{22}
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 5.--The momentum autocorrelation functions $\Psi_{31}(\tau)$ (solid line) and $\Psi(\tau)_{32}$ (dashed line) versus τ ($t \times 10^{12}$) from Eqs. (371) and (369) respectively for $D = 2.43 \times 10^{-5}$ cm^2/sec and $\langle \nabla^2 V \rangle = 11.0 \times 10^3 \frac{\text{ergs}}{\text{cm}^2}$.



1.0
.8
.6
.4
.2
0
-.2
ψ 1 ξ ψ32 (τ)
ψ31
ψ32
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 6.--The momentum correlation functions $\Psi_{41}(\tau)$ (solid line) and $\Psi_{42}(\tau)$ (dashed line) versus τ (t x 10^{12}) from Eqs. (371) and (369) for D = 2.72 x 10^{-5} cm^2/sec and $\langle \nabla^2 V \rangle = 11.0 \times 10^3 \frac{\text{ergs}}{\text{cm}^2}$.

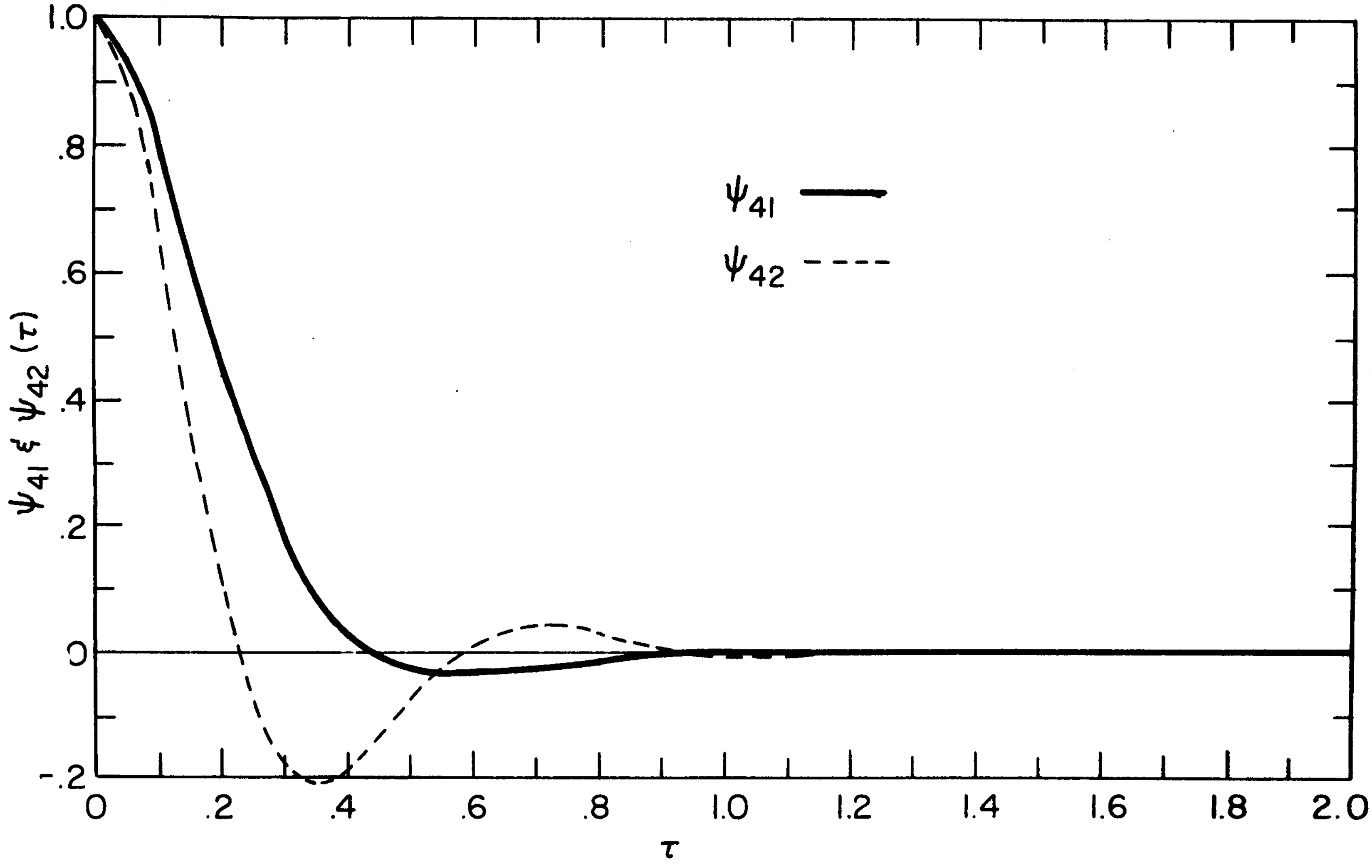
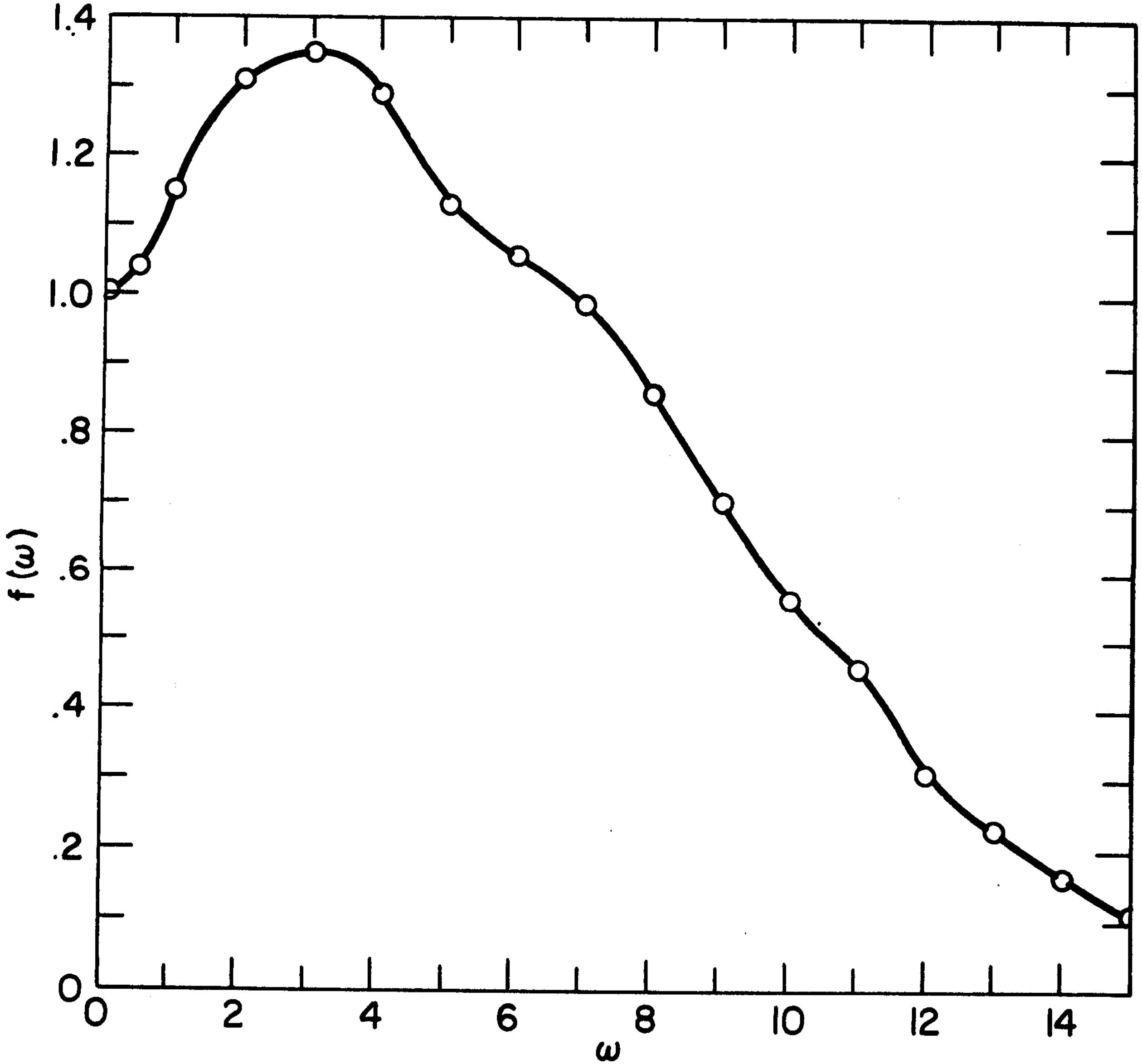

1.0
.8
.6
.4
.2
0
-.2
ψ41 ξ ψ42 (τ)
ψ41
ψ42
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 7.--The power spectrum (Eq. (415)) $f(\omega)$ versus ω from Rahman's computer experiment.



1.4
1.2
1.0
.8
.6
.4
.2
0
f (ω)
0
2
4
6
8
10
12
14
ω

Fig. 8.--The power spectrum (Eq. (415)) $f(\omega)$ versus ω in the Markovian approximation.

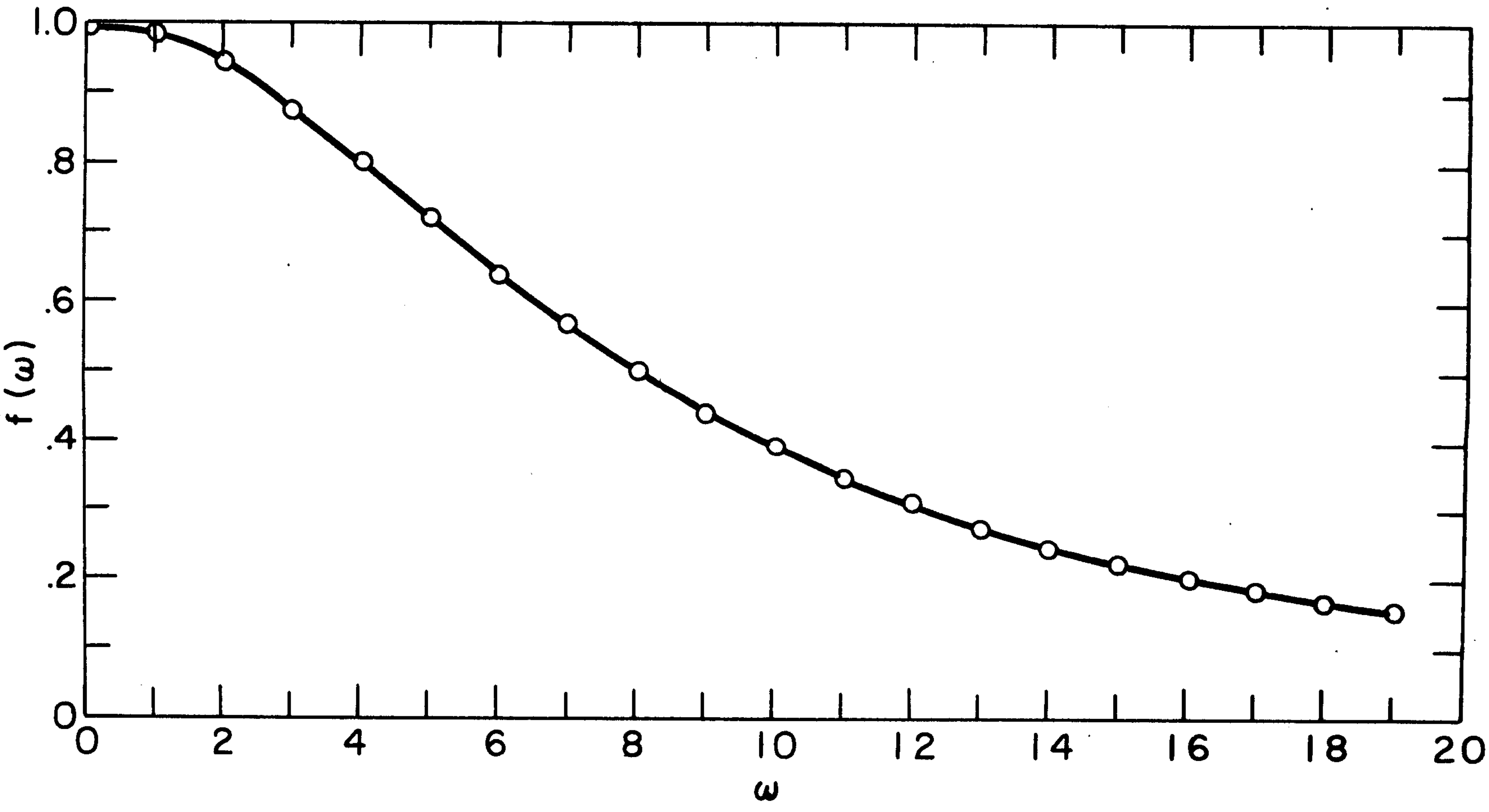
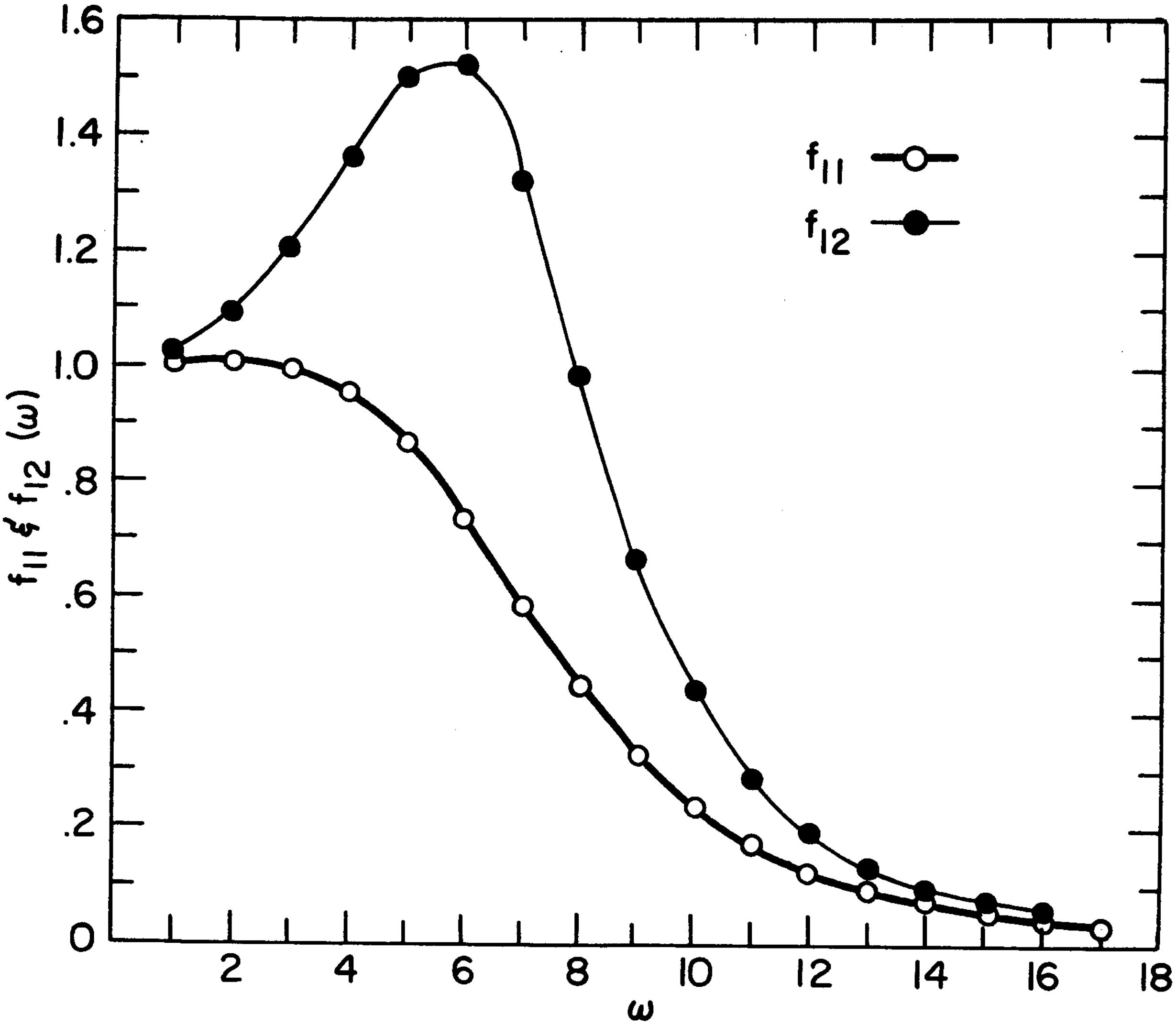
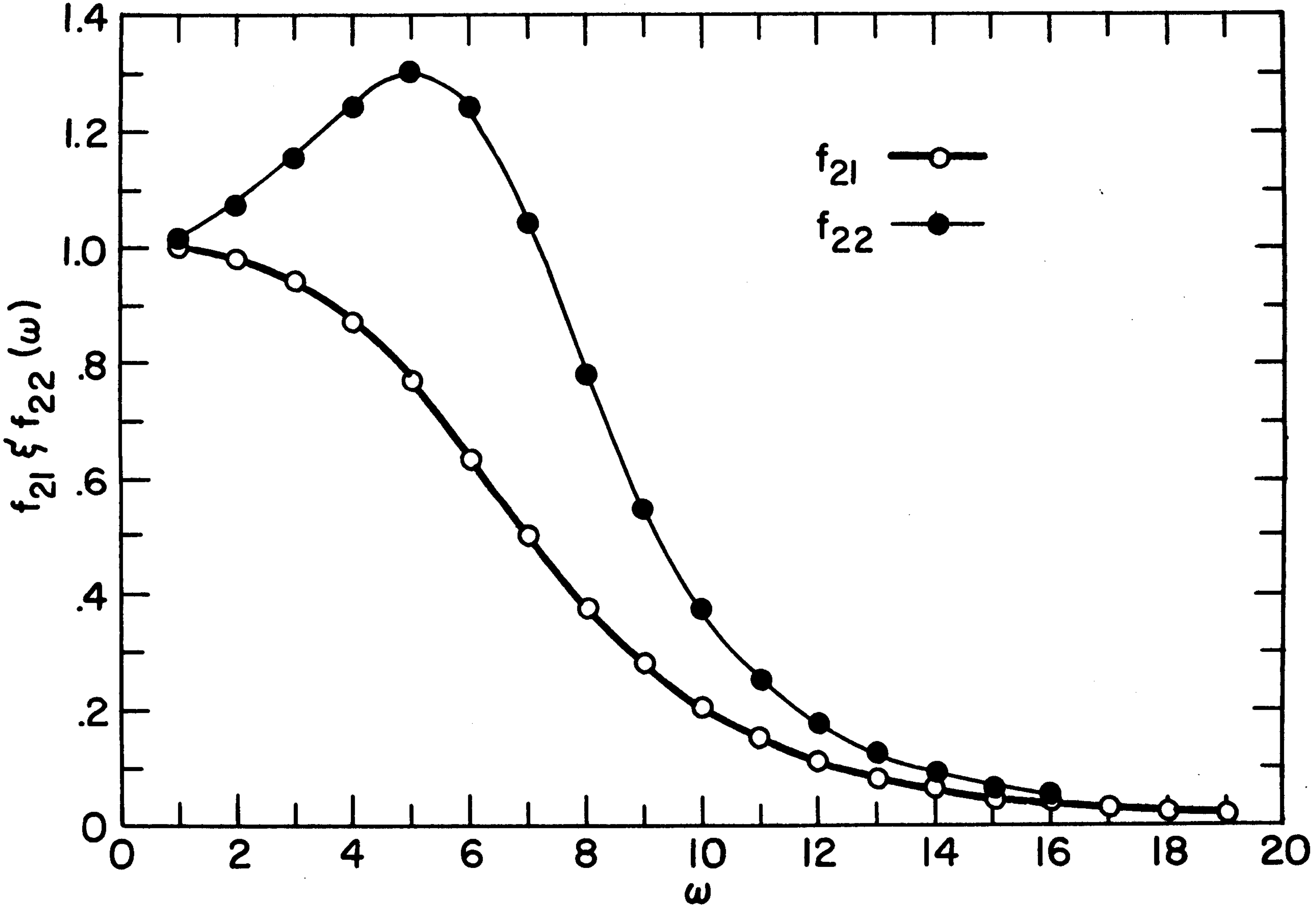

1.0
.8
.6
.4
.2
0
f (ω)
0
2
4
6
8
10
12
14
16
18
20
ω

Fig. 9.--The power spectrum (Eq. (415)), $f_{11}(\omega)$ (circles) and $f_{12}(\omega)$ (dots) versus ω, for $D = 2.43 \times 10^{-5}$ cm^2/sec and $\langle \nabla^2 V \rangle = 10.7 \times 10^3 \frac{ergs}{cm^2}$.



1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
f_{11} ¢ f_{12} (ω)
2
4
6
8
10
12
14
16
18
ω
f_{11}
f_{12}

Fig. 10.--The power spectra (Eq. (415)), $f_{21}(\omega)$ (circles) and $f_{22}(\omega)$ (dots) versus ω, for $D = 2.72 \times 10^{-5}$ cm^2/sec and $\langle \nabla^2 V \rangle = 10.7 \times 10^3 \frac{\text{ergs}}{\text{cm}^2}$.



f_{21}
f_{22}
f_{21} & f_{22} (ω)
ω
0
.2
.4
.6
.8
1.0
1.2
1.4
0
2
4
6
8
10
12
14
16
18
20

Fig. 11.--The power spectra (Eq. (415)) $f_{31}(\omega)$ (circles) and $f_{32}(\omega)$ (dots) versus ω for D = 2.43 x 10^{-5} cm^2/sec and $\langle \nabla^2 V \rangle = 11.0 \times 10^3 \frac{\text{ergs}}{\text{cm}^2}$.

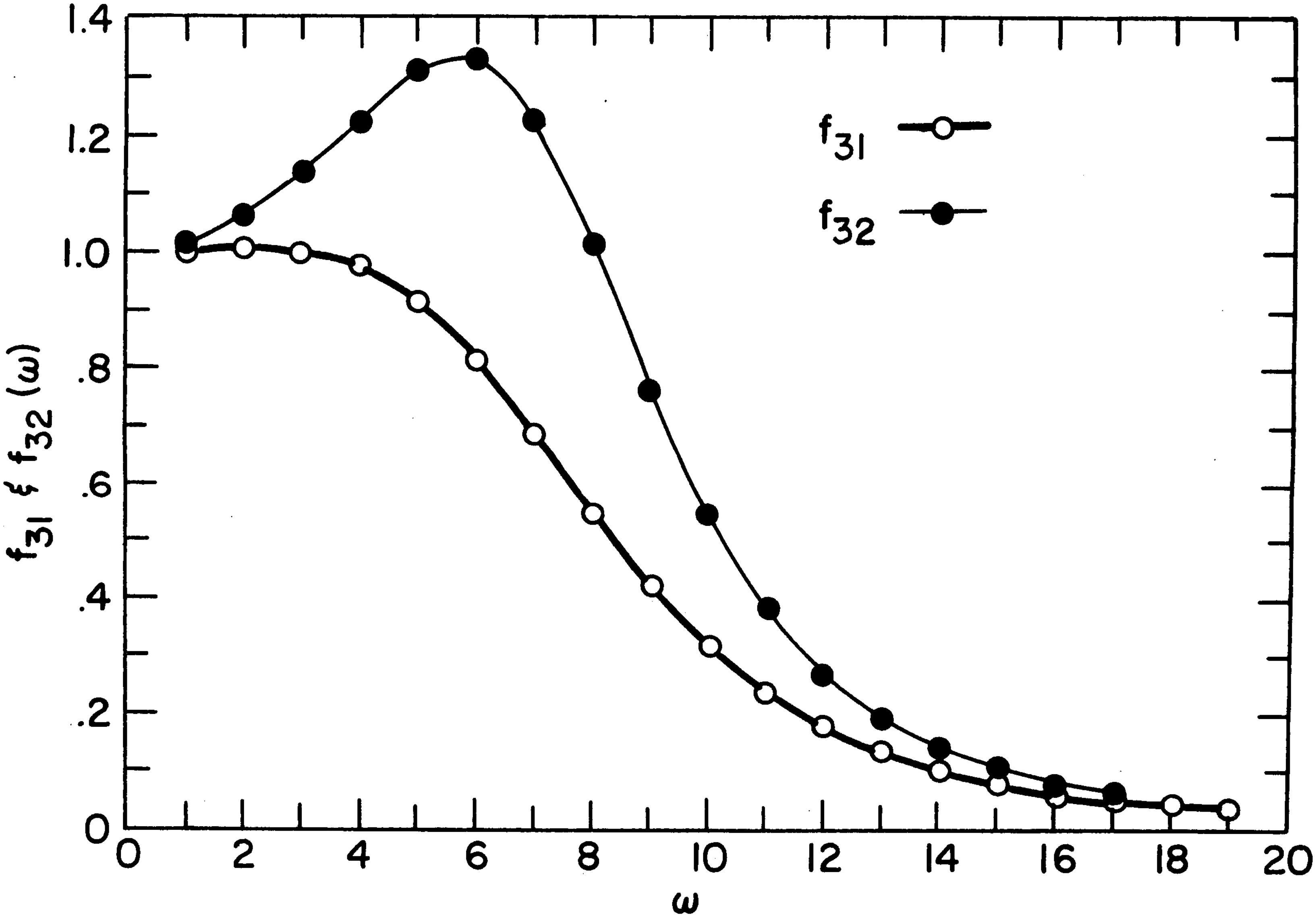
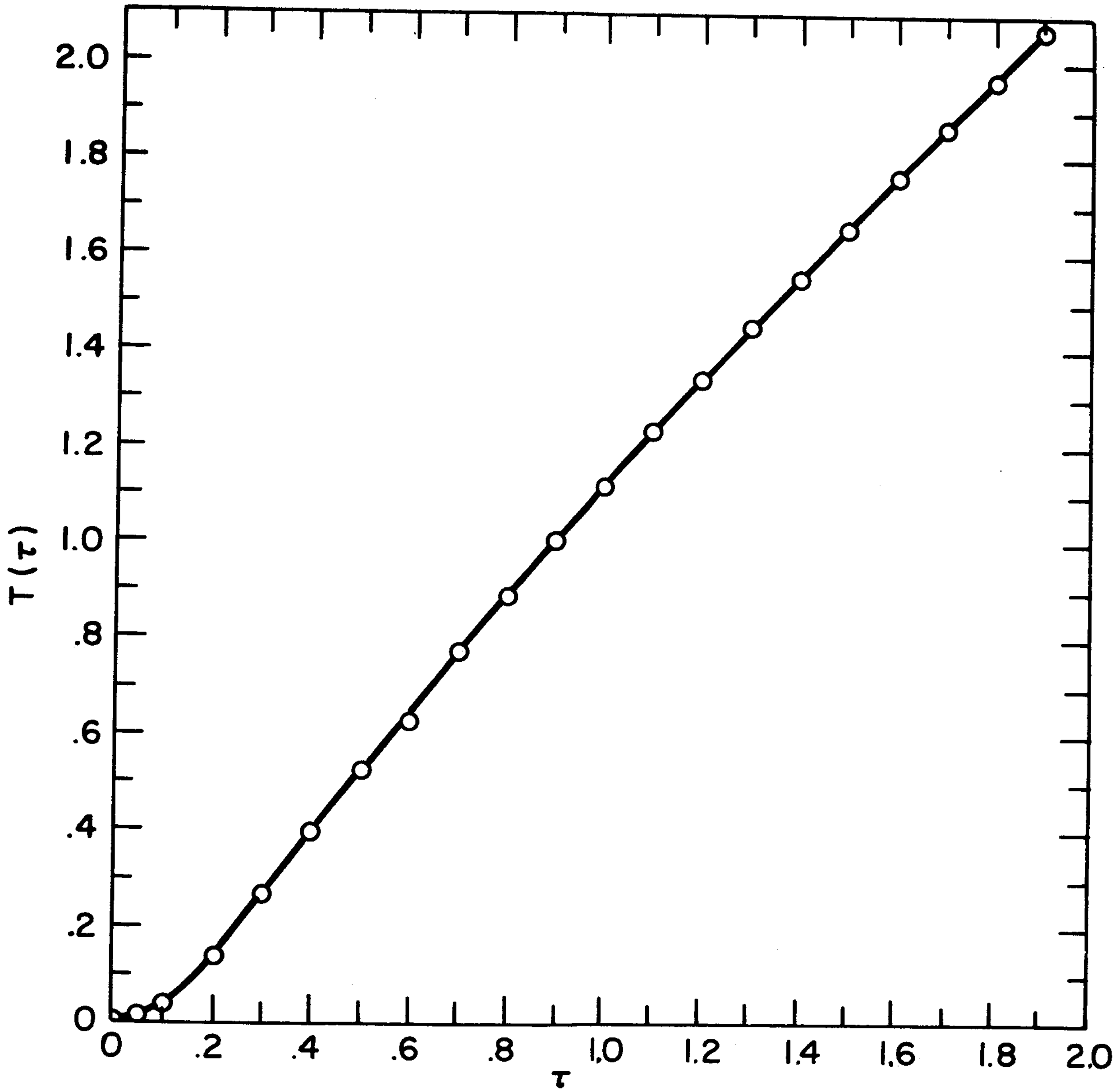

1.4
1.2
1.0
.8
.6
.4
.2
0
f_{31} ₤ f_{32} (ω)
0
2
4
6
8
10
12
14
16
18
20
ω
f_{31}
f_{32}

Fig. 12.--The mean square displacement (Eq. (451)) $T(\tau)$ versus τ from Rahman's computer experiment.



2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
T(τ)
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 13.--The mean square displacement (Eq. (451)) $T(\tau)$ versus τ in the Markovian approximation.

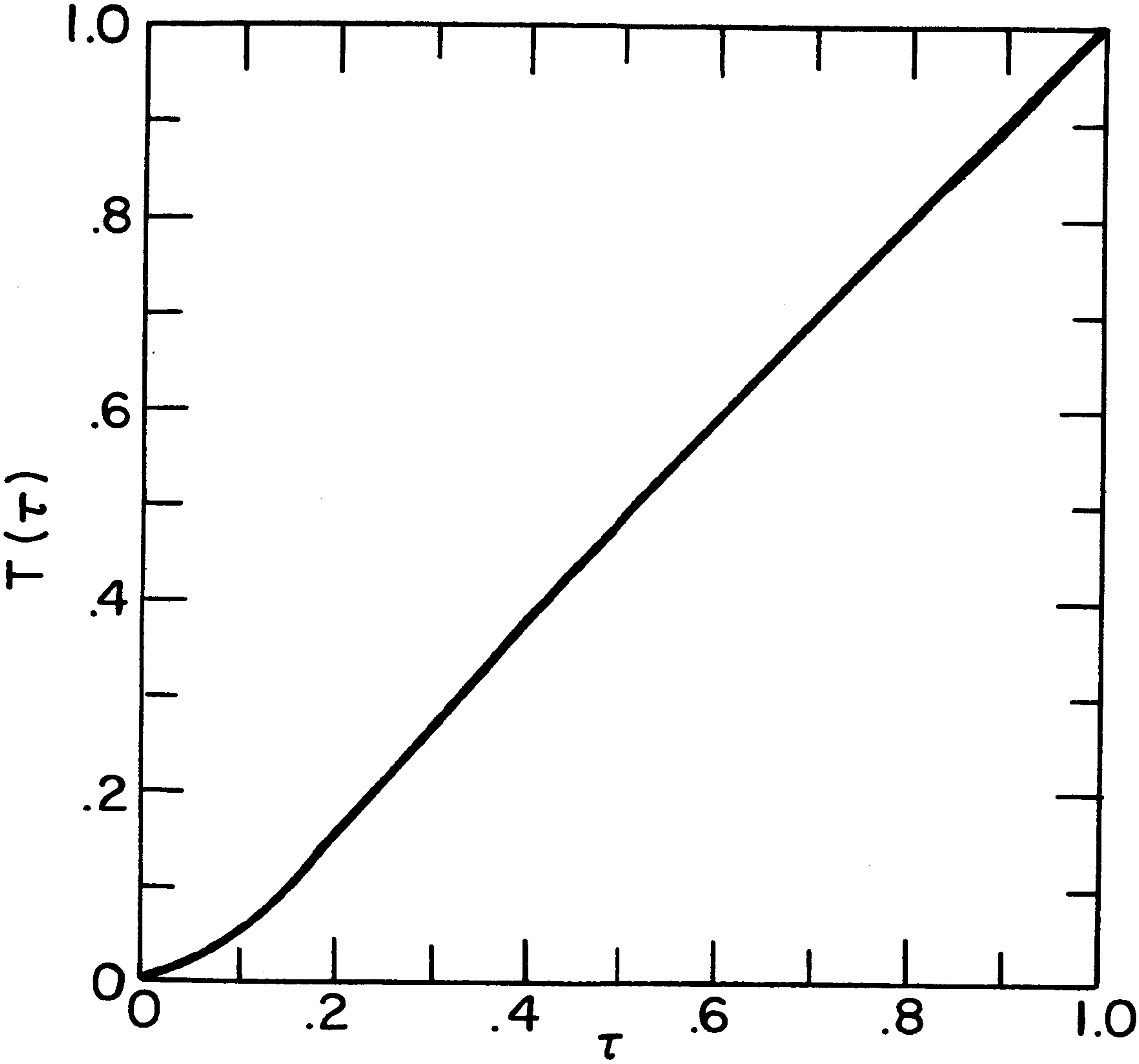
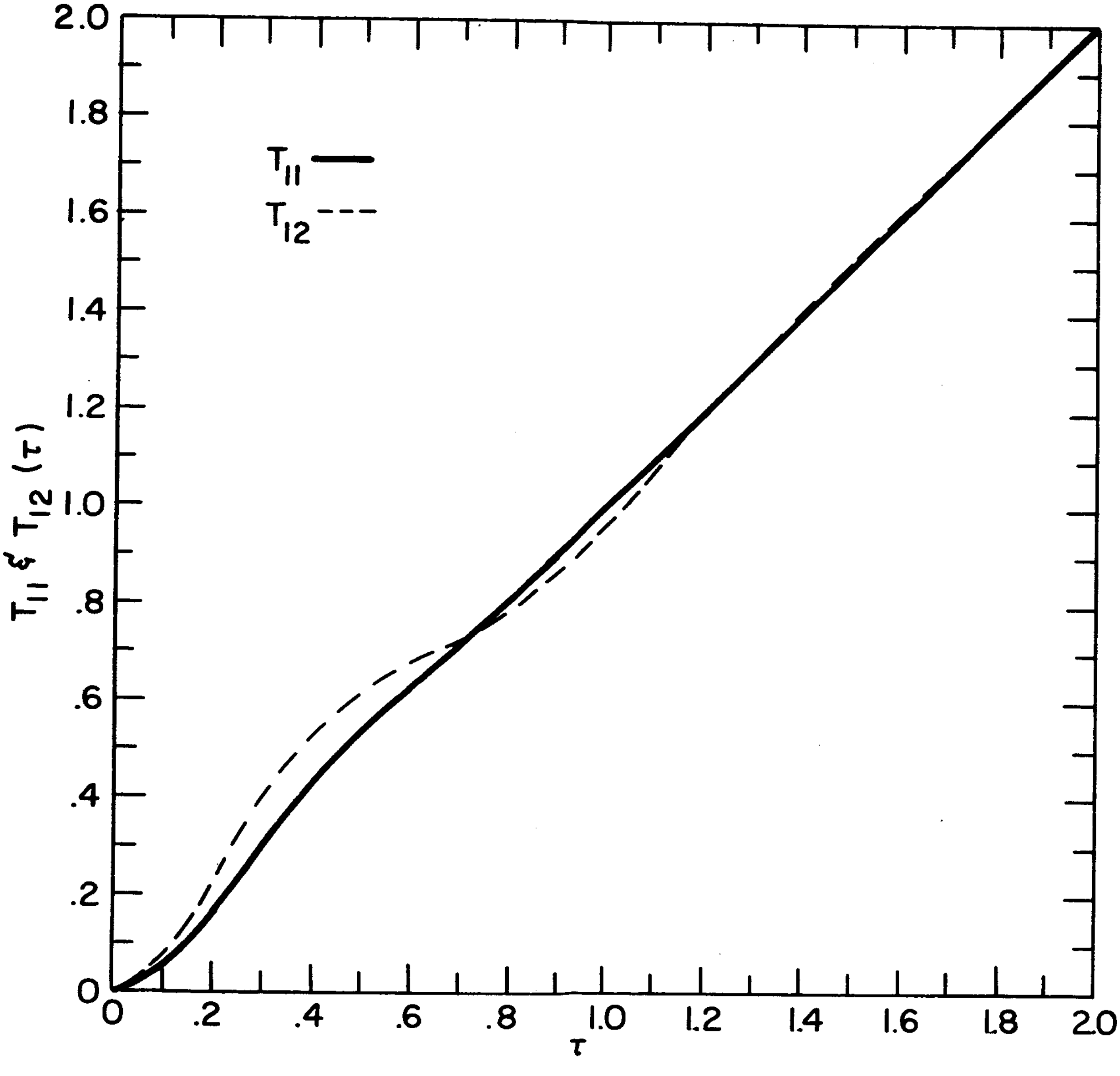
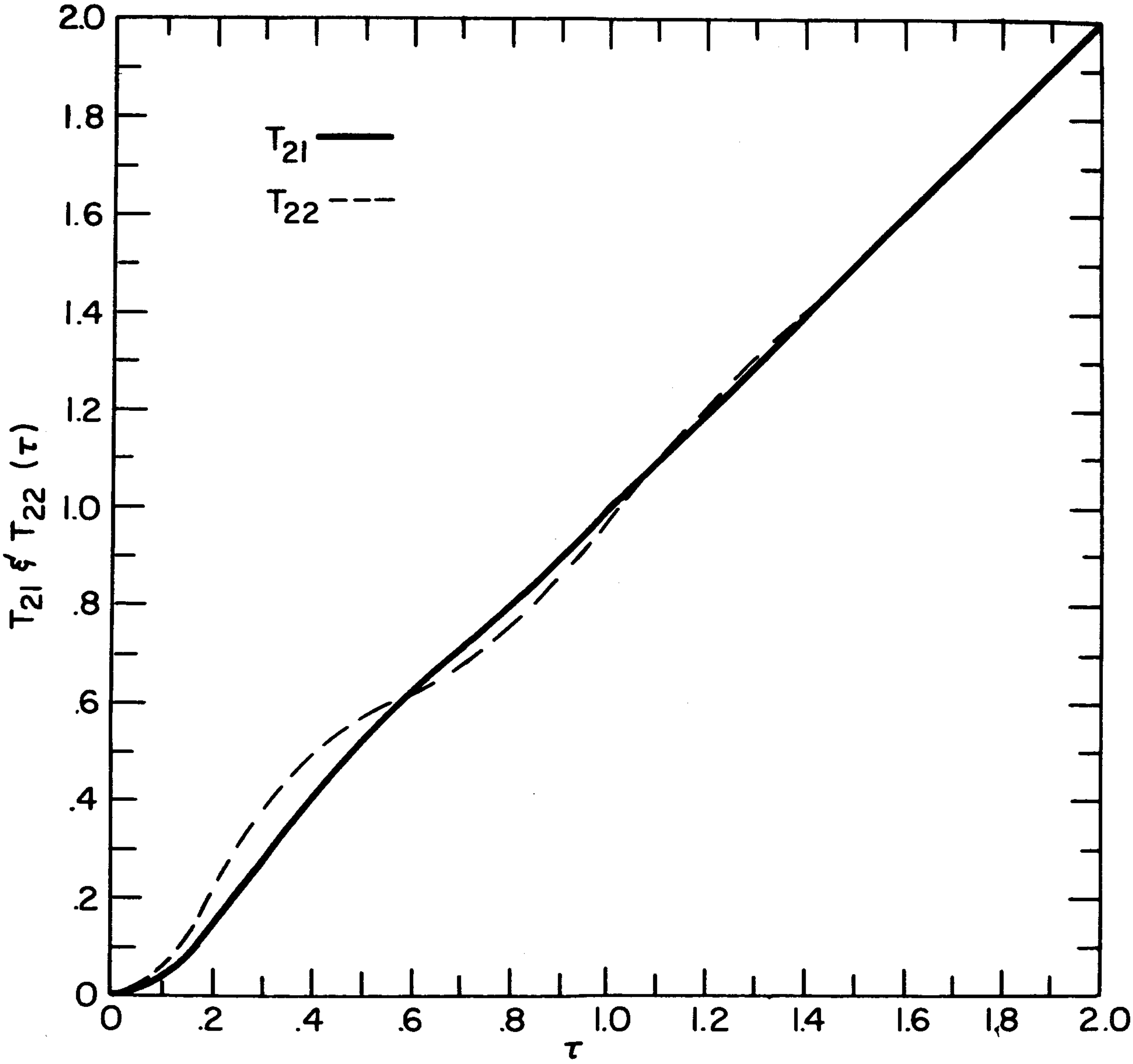

1.0
.8
.6
.4
.2
0
T (τ)
0
.2
.4
.6
.8
1.0
τ

Fig. 14.--The mean square displacement (Eq. (451)) $T_{11}(\tau)$ (solid line) and $T_{12}(\tau)$ (dashed line) versus τ from Eqs. (371) and (369) respectively for $D = 2.43 \times 10^{-5}$ cm^2/sec and $\langle \nabla^2 V \rangle = 10.7 \times 10^{-3} \frac{ergs}{cm^2}$.



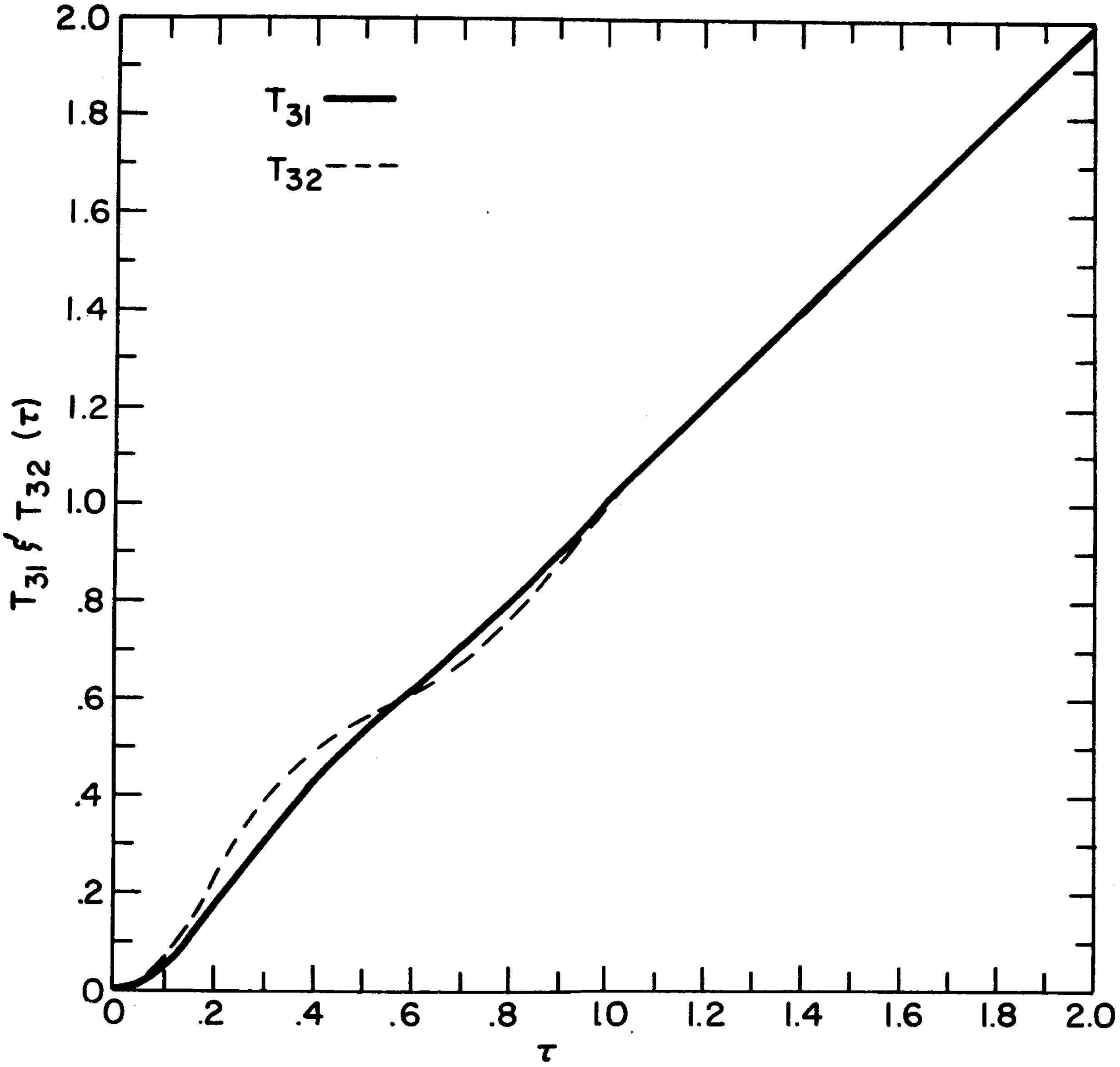
T_{11}
T_{12}
T_{11} & T_{12} (τ)
τ
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0

Fig. 15.--The mean square displacement (Eq. (451)) $T_{21}(\tau)$ (solid line) and $T_{22}(\tau)$ (dashed line) versus τ from Eqs. (371) and (369) respectively for $D = 2.72 \times 10^{-5}$ cm^2/sec and $\langle \nabla^2 V \rangle = 10.7 \times 10^3 \frac{\text{ergs}}{\text{cm}^2}$.



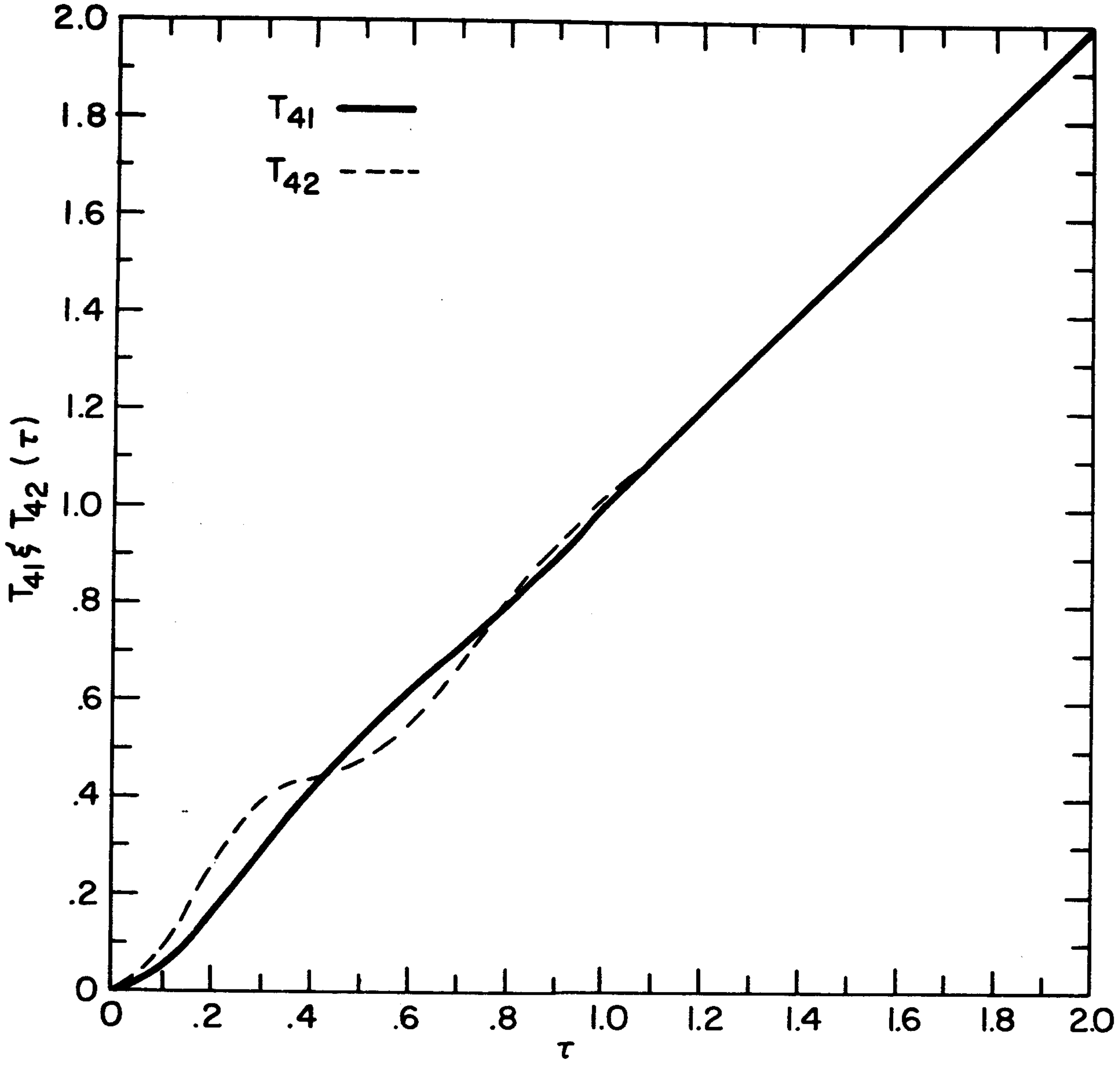
T_{21}
T_{22}
T_{21} & T_{22} (τ)
τ
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0

Fig. 16.--The mean square displacement (Eq. (451)) $T_{31}(\tau)$ (solid line) and $T_{32}(\tau)$ dashed line) versus τ from Eqs. (371) and (369) respectively for $D = 2.43 \times 10^{-5}\,cm^2/sec$ and $\langle \nabla^2 V \rangle = 11.0 \times 10^{+3} \frac{ergs}{cm^2}$.



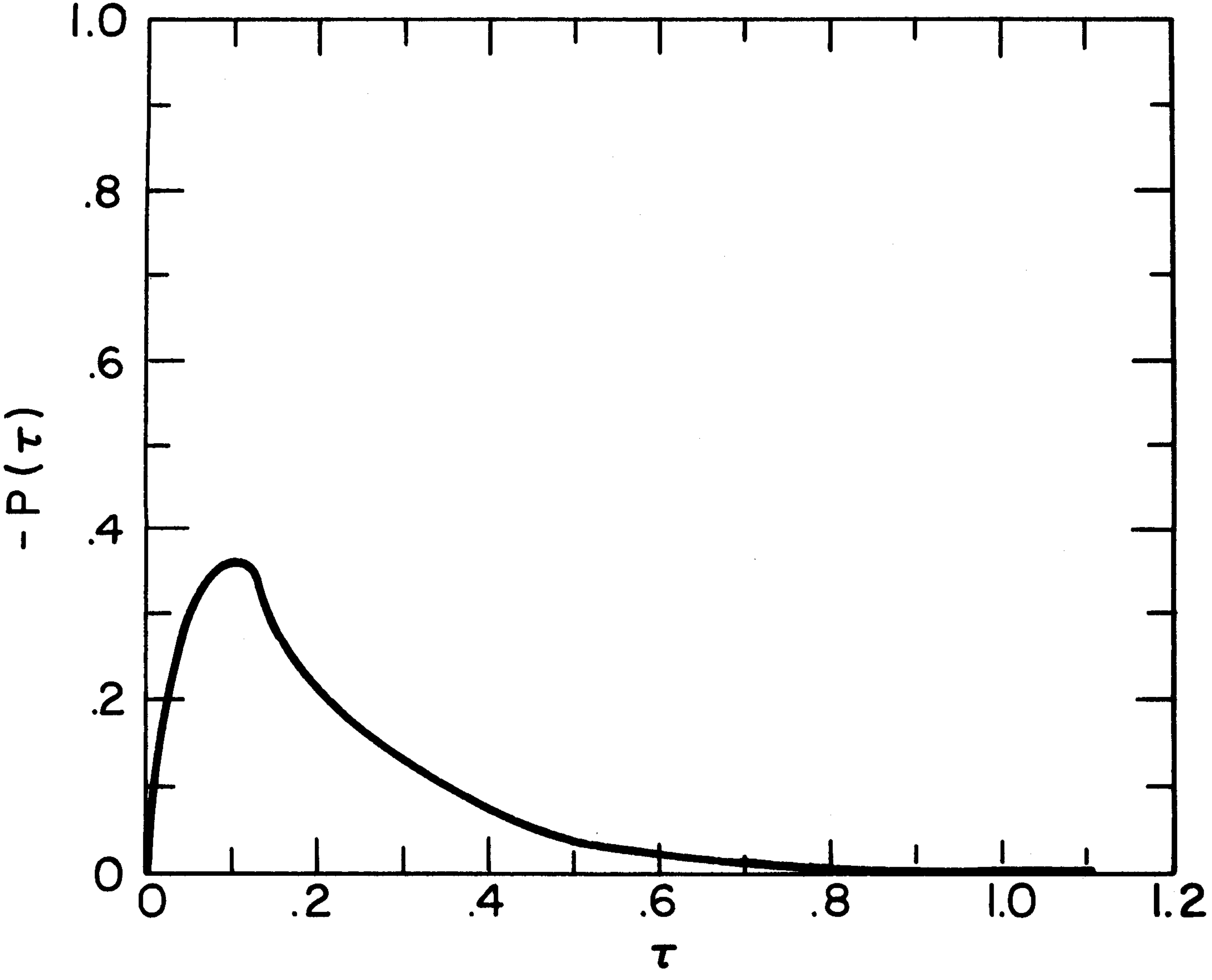
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
T_{31}
T_{32}
T_{31} & T_{32} (τ)
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 17.--The mean square displacement (Eq. (451) $T_{41}(\tau)$ (solid line) and $T_{42}(\tau)$ (dashed line) versus τ from Eqs. (371) and (369) respectively for $D = 2.72 \times 10^{-5}$ cm^2/sec and $\langle \nabla^2 V \rangle = 11.0 \times 10^{3} \ \frac{ergs}{cm^2}$.



T_{41}
T_{42}
T_{41} & T_{42} (τ)
τ
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0

Fig. 18.--The second moment of the momentum (Eq. (452)) $-P(\tau)$ versus τ in the Markovian approximation.



1.0
.8
.6
.4
.2
0
-P(τ)
0
.2
.4
.6
.8
1.0
1.2
τ

Fig. 19.--The second moment of the momentum (Eq. (452)) $-P_{11}(\tau)$ versus τ from Eq. (471) for D = 2.43 x 10^{-5} cm^2/sec and $\langle \nabla^2 V \rangle$ = 10.7 x 10^{+3} $\frac{\text{ergs}}{\text{cm}^2}$.

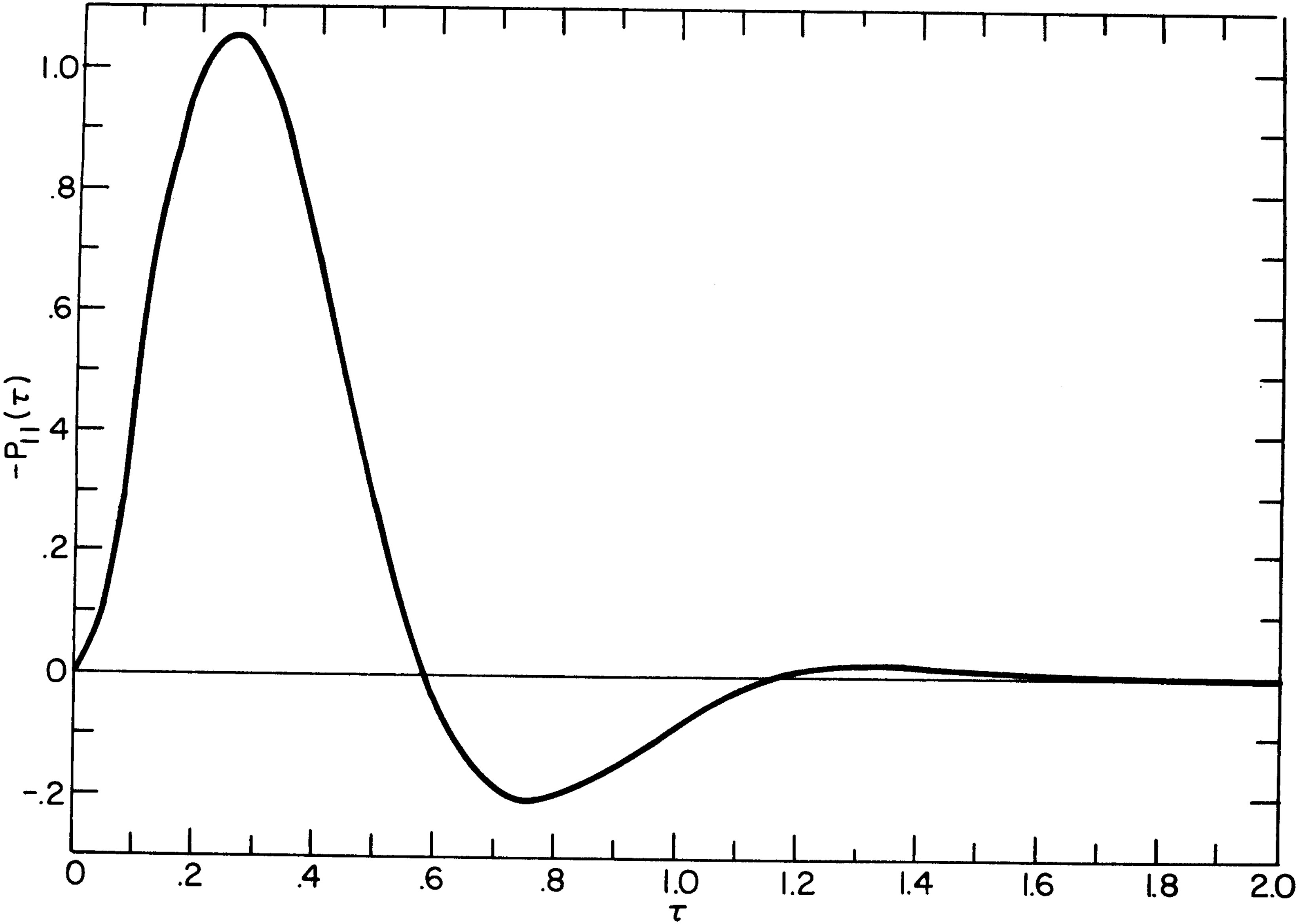
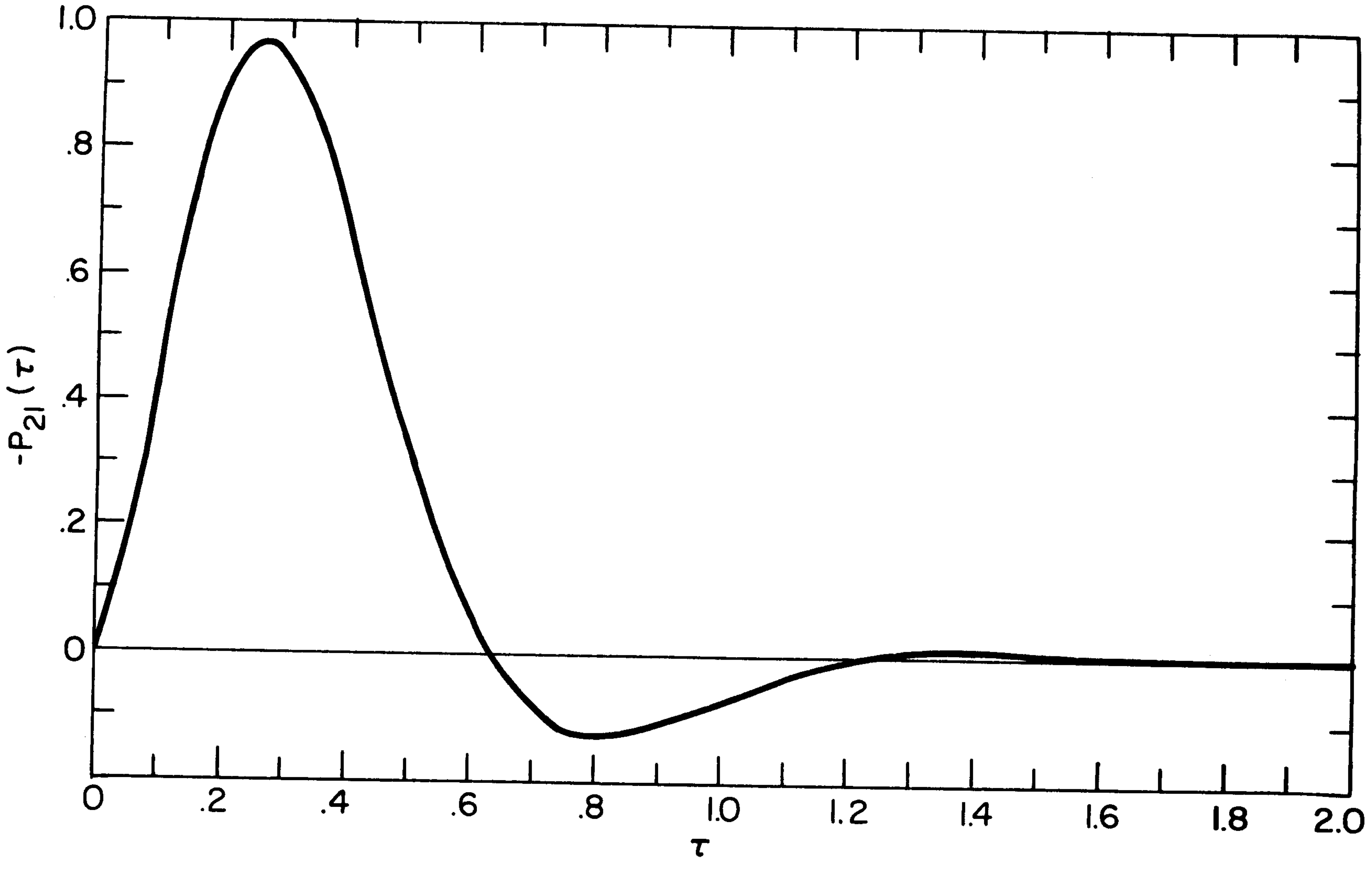
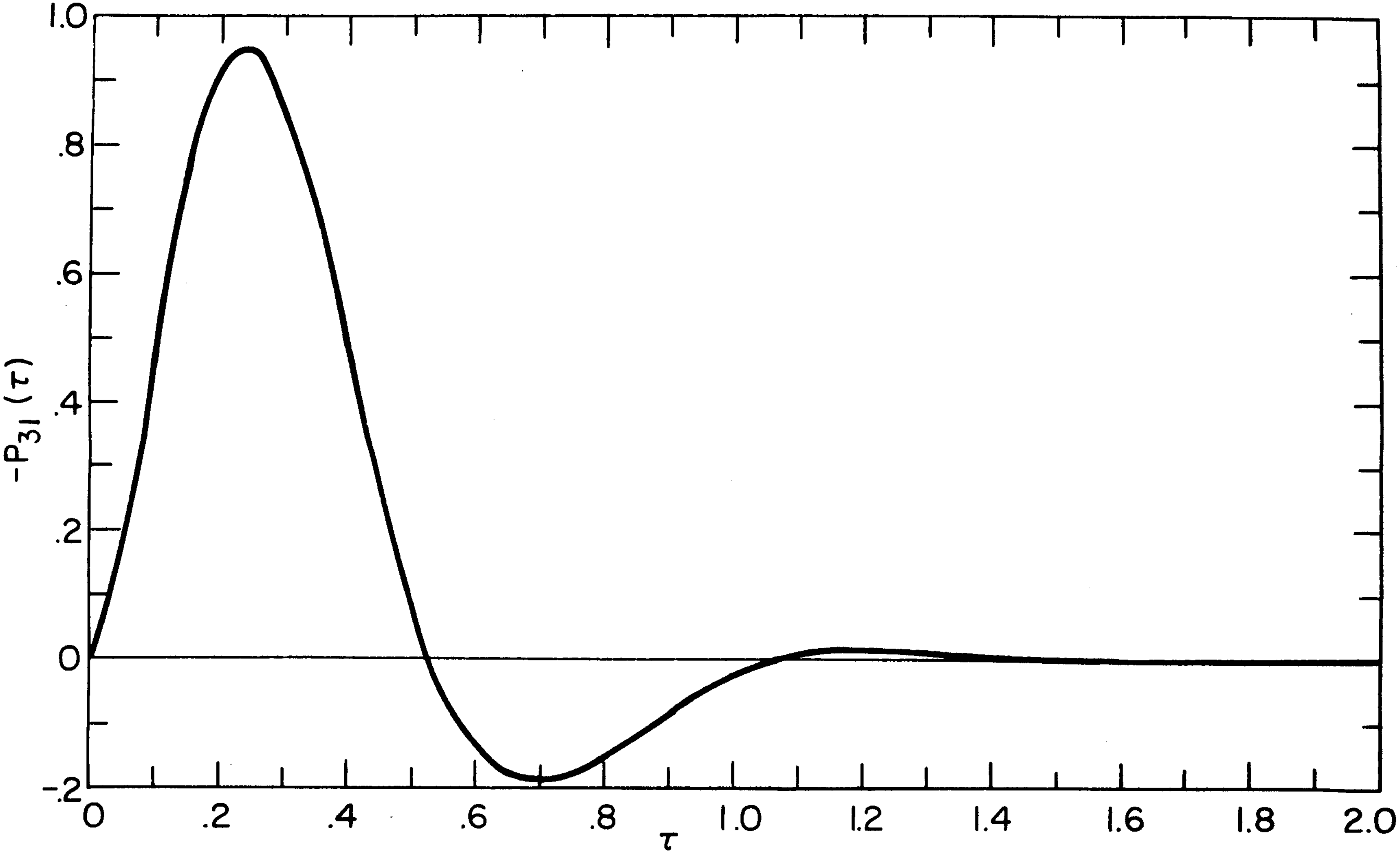

1.0
.8
.6
4
.2
0
-.2
$-P_{11}(\tau)$
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 20.--The second moment of the momentum (Eq. (452)) $-P_{21}(\tau)$ versus τ from Eq. (471) for $D = 2.72 \times 10^{-5}\ cm^2/sec$ and $\langle \nabla^2 V \rangle = 10.7 \times 10^3 \frac{ergs}{cm^2}$.



1.0
.8
.6
.4
.2
0
$-P_{21}(\tau)$
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 21.--The second moment of the momentum (Eq. (452)) $-P_{31}(\tau)$ versus τ from Eq. (471) for $D = 2.43 \times 10^{-5}$ cm^2/sec and $\langle \nabla^2 V \rangle = 11.0 \times 10^3 \frac{ergs}{cm^2}$.



1.0
.8
.6
.4
.2
0
-.2
$-P_{31}(\tau)$
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 22.--The second moment of the momentum (Eq. (452)) $-P_{41}(\tau)$ versus τ from Eq. (471) for $D = 2.72 \times 10^{-5}$ cm^2/sec and $\langle \nabla^2 V \rangle = 11.0 \times 10^3 \frac{\text{ergs}}{\text{cm}^2}$.

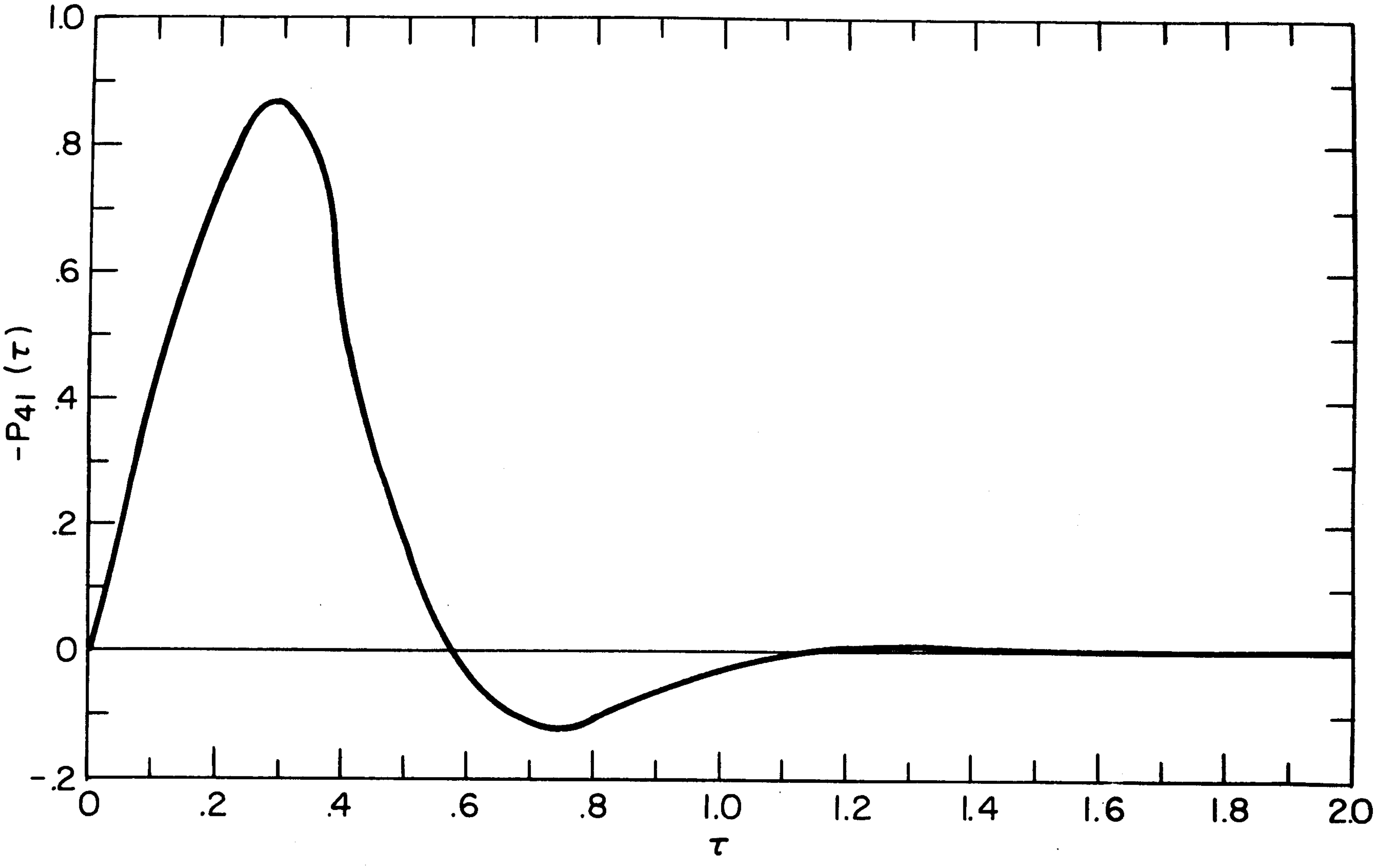
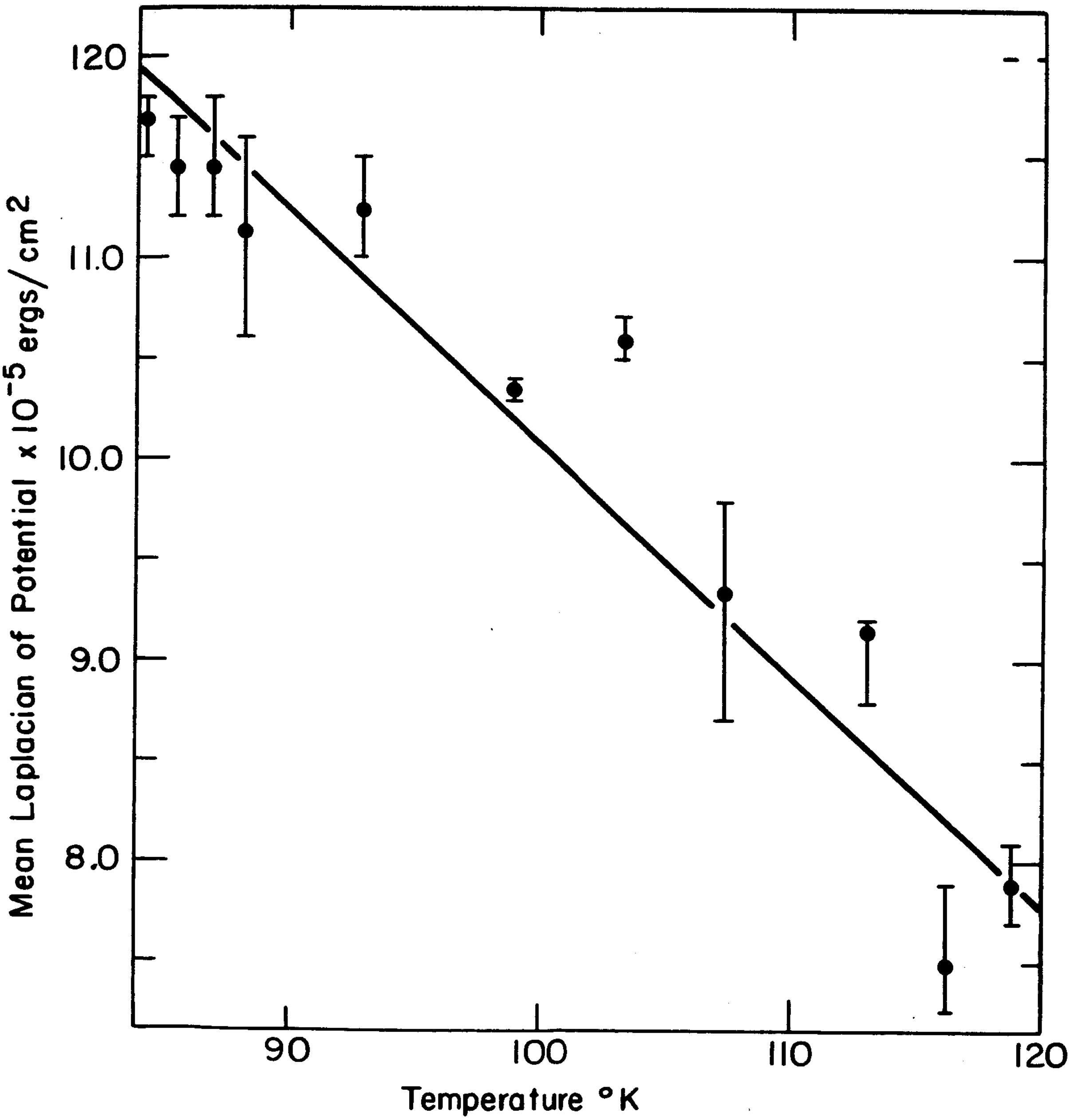

1.0
.8
.6
.4
.2
0
-.2
$-P_{41}(\tau)$
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
τ

Fig. 23.--The mean Laplacian of the potential as a function of temperature from isotope separation data.



120
11.0
10.0
9.0
8.0
Mean Laplacian of Potential x 10⁻⁵ ergs/cm²
90
100
110
120
Temperature °K

APPENDIX

DERIVATION OF THE INTEGRO-DIFFERENTIAL EQUATIONS FOR THE SINGLET AND DOUBLET DISTRIBUTION FUNCTIONS

In this Appendix we derive the integro-differential equations for the singlet and doublet distribution functions of an ideal inoic melt, on the basis of the Rice-Allnatt theory of transport in liquids. The properties of the model melt are described in sections 2 and 3 of chapter III.

We proceed by first deriving an equation for a binary mixture, and then specializing to the case of the ideal ionic melt.

Using the definition of the n body distribution function

$$f^{(n)}(\underline{R}_\alpha^{(n)}, \underline{R}_\beta^{(s)}, \underline{P}_\alpha^{(n)}, \underline{P}_\beta^{(s)}) = \left[(N_\alpha - m)!\,(N_\beta - s)!\right] \times \int\cdots\int f^{(N)}(\underline{R}^{(N)}, \underline{P}^{(N)})\, d\underline{R}^{(N-n)}\, d\underline{P}^{(N-n)} \tag{453}$$

and the Liouville equation,

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{j=1}^{N_\alpha} \left[\frac{1}{m_\alpha} \underline{P}_{\alpha j} \cdot \nabla_{R_{\alpha j}} + (\underline{F}_{\alpha j} + \underline{X}_{\alpha j}) \cdot \nabla_{P_{\alpha j}} \right] f^{(N)}$$

$$+ \sum_{K=1}^{N_\beta} \left[\frac{1}{m_\beta} \underline{P}_{\beta K} \cdot \nabla_{R_{\beta K}} + (\underline{F}_{\beta K} + \underline{X}_{\beta K}) \cdot \nabla_{P_{\beta K}} \right] f^{(N)} = 0 \tag{454}$$

it is readily found that

$$(N_\alpha - 1)!\, N_\beta! \left[\frac{\partial \bar{f}^{(1)}(\alpha 1)}{\partial t} + \frac{1}{m_\alpha} \underline{P}_{\alpha 1} \cdot \nabla_{R_{\alpha 1}} \bar{f}^{(1)}(\alpha 1) + \underline{X}_{\alpha 1} \cdot \nabla_{P_{\alpha 1}} \bar{f}^{(1)}(\alpha 1) \right]$$

$$+ \sum_{j=1}^{N_\alpha} \int \cdots \int \underline{F}_{\alpha j} \cdot \nabla_{P_{\alpha j}} f^{(N)} \, d\underline{R}_\alpha^{(N-1)} \, d\underline{P}_\alpha^{(N-1)} \tag{455}$$

$$+ \sum_{K=1}^{N_\beta} \int \cdots \int \underline{F}_{\beta K} \cdot \nabla_{P_{\beta K}} f^{(N)} \, d\underline{R}_\alpha^{(N-1)} \, d\underline{P}_\alpha^{(N-1)} = 0$$

where

$$d\underline{R}_\alpha^{(N-1)} \, d\underline{P}_\alpha^{(N-1)} = \prod_{j=2}^{N_\alpha} d\underline{R}_{\alpha j} \, d\underline{P}_{\alpha j} \prod_{K=1}^{N_\beta} d\underline{R}_{\beta K} \, d\underline{P}_{\beta K} . \tag{456}$$

It is convenient to define

$$I_j = \int \cdot\cdot \int \underset{\sim}{F}_{\alpha j} \cdot \nabla_{P_{\alpha j}} f^{(N)} d\underset{\sim}{R}_\alpha^{(N-1)} d\underset{\sim}{P}_\alpha^{(N-1)}$$

$$J_K = \int \cdot\cdot \int \underset{\sim}{F}_{\beta K} \cdot \nabla_{P_{\beta K}} f^{(N)} d\underset{\sim}{R}_\alpha^{(N-1)} d\underset{\sim}{P}_\alpha^{(N-1)} \tag{457}$$

For a pairwise additive intermolecular potential,

$$\underset{\sim}{F}_{\alpha j} = \sum_{i \neq j}^{N_\alpha} \underset{\sim}{F}_{\alpha j, \alpha i} + \sum_{K=1}^{N_\beta} \underset{\sim}{F}_{\alpha j, \beta K} \tag{458}$$

$$\underset{\sim}{F}_{\beta K} = \sum_{j=1}^{N_\alpha} \underset{\sim}{F}_{\beta K, \alpha j} + \sum_{\ell \neq K}^{N_\beta} \underset{\sim}{F}_{\beta K, \beta \ell}, \tag{459}$$

whereupon with the use of (458) and (459) in Eq. (457) and integration with respect to $d\underset{\sim}{R}_\alpha^{(N-1)} d\underset{\sim}{R}_\alpha^{(N-1)}$, it is found that

$$\sum_{j=1}^{N_\alpha} I_j = (N_\alpha - 1)!\, N_\beta! \int \cdot\cdot \int \underset{\sim}{F}_{\alpha 1, \alpha 2} \cdot \nabla_{P_{\alpha 1}} f^{(2)}(\alpha 1, \alpha 2; t+s)\, d\underset{\sim}{R}_{\alpha 2} d\underset{\sim}{P}_{\alpha 2}$$

$$+ (N_\alpha - 1)!\, N_\beta! \int \cdot\cdot \int \underset{\sim}{F}_{\alpha 1, \beta 1} \cdot \nabla_{P_{\alpha 1}} f^{(2)}(\alpha 1, \alpha 2; t+s)\, d\underset{\sim}{R}_{\beta 1} d\underset{\sim}{P}_{\beta 1}\,. \tag{460}$$

We note that $J_k = 0$ for all k because we are integrating over the entire phase space of component β. Thus, combining Eqs. (455) and (460)

$$\frac{\partial f^{(1)}(\alpha 1)}{\partial t} + \frac{1}{m_\alpha}\underline{P}_{\alpha 1}\cdot\nabla_{R_{\alpha 1}} f^{(1)}(\alpha 1) + \underline{X}_{\alpha 1}\cdot\nabla_{P_{\alpha 1}} f^{(1)}(\alpha 1)$$

$$= -\int\cdots\int \underline{F}_{\alpha 1,\alpha 2}\cdot\nabla_{P_{\alpha 1}} f^{(2)}(\alpha 1,\alpha 2)\, d\underline{R}_{\alpha 2}\, d\underline{P}_{\alpha 2}$$

$$- \int\cdots\int \underline{F}_{\alpha 1,\beta 1}\cdot\nabla_{P_{\alpha 1}} f^{(2)}(\alpha 1,\beta 1)\, d\underline{R}_{\beta 1}, d\underline{P}_{\beta 1} \; . \tag{461}$$

Of course Eq. (461) contains all the information inherent in the Liouville equation because $\bar{f}^{(2)}$ must be found from $\bar{f}^{(3)}$ and $\bar{f}^{(3)}$ from $\bar{f}^{(4)}$ etc. The basic assumption used to truncate the hierarchy is that of Rice and Allnatt. The formal procedure involves the introduction of time smoothing. We define a coarse-grained distribution function

$$\bar{f}^{(N)} = \frac{1}{\tau}\int_0^\tau f^{(N)}(\underline{R}^{(N)}, \underline{P}^{(N)}; t+s)\, ds, \tag{462}$$

where τ is the interval of coarse graining. If Eq. (461) is time smoothes, one finds

$$\frac{\partial \bar{f}^{(1)}(\alpha 1)}{\partial t} + \frac{1}{m_\alpha}\underline{p}_{\alpha 1}\cdot\nabla_{R_{\alpha 1}}\bar{f}^{(1)}(\alpha 1) + \underline{X}_{\alpha 1}\cdot\nabla_{p_{\alpha 1}}\bar{f}^{(1)}(\alpha 1)$$

$$= -\tau^{-1}\int_0^\tau\cdots\int \underline{F}_{\alpha 1,\alpha 2}\cdot\nabla_{p_{\alpha 1}} f^{(2)}(\alpha 1,\alpha 2;t+s)\,ds\,d\underline{R}_{\alpha 2}\,d\underline{p}_{\alpha 2} \tag{463}$$

$$-\tau^{-1}\int_0^\tau\cdots\int \underline{F}_{\alpha 1,\beta 1}\cdot\nabla_{p_{\beta 1}} f^{(2)}(\alpha 1,\beta 1;t+s)\,ds\,d\underline{R}_{\beta 1}\,d\underline{p}_{\beta 1}.$$

Now, following Rice and Allnatt we subdivide the force on a particle into hard and soft components,

$$\underline{F}_{\alpha 1,\kappa 1} = \underline{F}^{(S)}_{\alpha 1,\kappa 1} + \underline{F}^{(R)}_{\alpha 1,\kappa 1}, \tag{464}$$

with the operator definition

$$\mathcal{L}_{\alpha 1} = \frac{\partial}{\partial t} + \frac{1}{m_\alpha}\underline{p}_{\alpha 1}\cdot\nabla_{R_{\alpha 1}} + \underline{X}_{\alpha 1}\cdot\nabla_{p_{\alpha 1}}. \tag{465}$$

Equation (463) assumes the form

$$\mathcal{L}_{\alpha 1}\bar{f}^{(1)}(\alpha 1) = -\tau^{-1}\int_0^\tau\cdots\int \underline{F}^{(R)}_{\alpha 1,\alpha 2}\cdot\nabla_{p_{\alpha 1}} f^{(2)}(\alpha 1,\alpha 2;t+s)\,ds\,d\underline{R}_{\alpha 2}\,d\underline{p}_{\alpha 2}$$

$$-\tau^{-1}\int_0^\tau\cdots\int \underline{F}^{(R)}_{\alpha 1,\beta 1}\cdot\nabla_{p_{\alpha 1}} f^{(2)}(\alpha 1,\beta 1;t+s)\,ds\,d\underline{R}_{\beta 1}\,d\underline{p}_{\beta 1}$$

$$-\tau^{-1}\int_0^\tau\cdots\int \underline{F}^{(S)}_{\alpha 1,\alpha 2}\cdot\nabla_{p_{\alpha 1}} f^{(2)}(\alpha 1,\alpha 2;t+s)\,ds\,d\underline{R}_{\alpha 2}\,d\underline{p}_{\alpha 2} \tag{466}$$

$$-\tau^{-1}\int_0^\tau\cdots\int \underline{F}^{(S)}_{\alpha 1,\beta 1}\cdot\nabla_{p_{\alpha 1}} f^{(2)}(\alpha 1,\beta 1;t+s)\,ds\,d\underline{R}_{\beta 1}\,d\underline{p}_{\beta 1}.$$

This may be written

$$\mathcal{L}_{\alpha 1} \bar{f}^{(1)}(\alpha 1) = \Omega_R^{\alpha 1} + \Omega_S^{\alpha 1}, \tag{467}$$

where the notation is obvious. For the ideal ionic melt only unlike ions undergo rigid-core encounters, whereupon

$$\Omega_R^{\alpha 1} = -\tau^{-1} \int_0^{\tau} \int \underline{F}^{(R)}_{\alpha 1, \beta 1} \cdot \nabla_{p_{\alpha 1}} \bar{f}^{(2)}(\alpha 1, \beta 1; t+s)\, ds\, d\underline{R}_{\beta 1} d\underline{P}_{\beta 1}; \tag{468}$$

whereas $\Omega_S^{\alpha 1}$ involves interactions with both α and β ions.

It is convenient at this point to introduce the Green's function (phase space transformation function) which has the property that

$$f^{(N)}(t+s) = \int \cdots \int K^{(N)}(\underline{R}^{(N)} \underline{P}^{(N)} | \underline{R}^{(N)'} \underline{P}^{(N)'}; s) f^{(N)}(t)\, d\underline{R}^{(N)'} d\underline{P}^{(N)'} \tag{469}$$

$$K^{(N)}(\underline{R}^{(N)} \underline{P}^{(N)} | \underline{R}^{(N)'} \underline{P}^{(N)'}; s) = \prod_{j=1}^{N_\alpha} \delta(\underline{R}_{\alpha j} - \underline{R}'_{\alpha j}) \delta(\underline{P}_{\alpha j} - \underline{P}'_{\alpha j}) \tag{470}$$

$$\times \prod_{K=1}^{N_\beta} \delta(R_{\beta K} - R'_{\beta K}) \delta(\underline{P}_{\beta K} - \underline{P}'_{\beta K}),$$

where the increments in momenta and coordinates must be computed from the complete N-body dynamics.

Green's functions corresponding to the reduced n body problem are obtained using the definitions

$$f^{(N)}(\underline{R}^{(N)}\underline{P}^{(N)}) = f^{(n|N-n)}(\underline{R}^{(N-n)}\underline{P}^{(N-n)})\, f^{(n)}(\underline{R}^{(n)}\underline{P}^{(n)}), \tag{471}$$

$$f^{(n)}(\underline{R}^{(n)}\underline{P}^{(n)};t+s) = \int\cdot\cdot\int K^{(n)}(\underline{R}^{(n)}\underline{P}^{(n)}|\underline{R}^{(n)'}\underline{P}^{(n)'};s)\, f^{(n)}(\underline{R}^{(n)'}\underline{P}^{(n)'};t)\, d\underline{R}^{(n)'}d\underline{P}^{(n)'} \tag{472}$$

$$K^{(n)}(\underline{R}^{(n)}\underline{P}^{(n)}|\underline{R}^{(n)'}\underline{P}^{(n)'};s) = \int\cdot\int K^{(N)}(\underline{R}^{(N)}\underline{P}^{(N)}|\underline{R}^{(N)'}\underline{P}^{(N)'};s) \tag{473}$$

$$\times\, f^{(n|N-n)}(\underline{R}^{(N-n)'}\underline{P}^{(N-n)'};t)\, d\underline{R}^{(N-n)'}d\underline{P}^{(N-n)'}.$$

Starting from the Liouville equation satisfied by $K^{(N)}$ equations for the two body Green's functions $K^{(2)}(\alpha 1, \alpha 2)$, $K^{(2)}(\alpha 1, \beta 1)$, and $K^{(2)}(\beta 1, \beta 2)$, may be found by integrating the Liouville equation with respect to all coordinates and momenta except those of (α1, α3), (α1, β1), and (β1, β2), respectively. We display only the equations (α1, β1), and (α1, α2) since the other is obtained by simple symmetry considerations.

$$\frac{\partial K^{(2)}(\alpha 1, \alpha 2)}{\partial s} + \frac{1}{m_\alpha} \underset{\sim}{P}_{\alpha 1} \cdot \nabla_{R_{\alpha 1}} K^{(2)} + \frac{1}{m_\alpha} \underset{\sim}{P}_{\alpha 2} \cdot \nabla_{R_{\alpha 2}} K^{(2)}$$

$$+ \underset{\sim}{F}_{\alpha 1, \alpha 2} \cdot \nabla_{P_{\alpha 1}} K^{(2)} + \underset{\sim}{F}_{\alpha 2, \alpha 1} \cdot \nabla_{P_{\alpha 2}} K^{(2)}$$

$$= - \int \cdots \int \sum_{j=3}^{N_\alpha} \left[\underset{\sim}{F}_{\alpha 1, \alpha j} \cdot \nabla_{P_{\alpha 1}} + \underset{\sim}{F}_{\alpha 2, \alpha j} \cdot \nabla_{P_{\alpha 2}} \right] K^{(N)} f^{(2/N-2)} d\underset{\sim}{R}^{(N-2)} d\underset{\sim}{P}^{(N-2)}$$

$$- \int \int \sum_{K=1}^{N_\beta} \left[\underset{\sim}{F}_{\alpha 1, \beta K} \cdot \nabla_{P_{\alpha 1}} + \underset{\sim}{F}_{\alpha 2, \beta K} \cdot \nabla_{P_{\alpha 2}} \right] K^{(N)} f^{(2/N-2)} d\underset{\sim}{R}^{(N-2)} d\underset{\sim}{P}^{(N-2)} ,$$

and

$$\frac{\partial K^{(2)}(\alpha 1, \beta 1)}{\partial s} + \frac{1}{m_\alpha} \underline{p}_{\alpha 1} \cdot \nabla_{R_{\alpha 1}} K^{(2)} + \frac{1}{m_\beta} \underline{p}_{\beta 1} \cdot \nabla_{R_{\beta 1}} K^{(2)}$$

$$+ \underline{F}_{\alpha 1, \beta 1} \cdot \nabla_{p_{\alpha 1}} K^{(2)} + \underline{F}_{\beta 1, \alpha 1} \cdot \nabla_{p_{\beta 1}} K^{(2)}$$

$$= - \int \cdots \int \sum_{j=2}^{N_\alpha} \left[F_{\alpha 1, \alpha j} \cdot \nabla_{p_{\alpha 1}} + F_{\beta 1, \alpha j} \cdot \nabla_{p_{\beta 1}} \right] K^{(N)} f^{(2|N-2)} d\underline{R}^{(N-2)} d\underline{p}^{(N-2)}$$

$$- \int \cdots \int \sum_{k=2}^{N_\beta} \left[\underline{F}_{\alpha 1, \beta k} \cdot \nabla_{p_{\alpha 1}} + \underline{F}_{\beta 1, \beta k} \cdot \nabla_{p_{\beta 1}} \right] K^{(N)} f^{(2|N-2)} d\underline{R}^{(N-2)} d\underline{p}^{(N-2)} .$$

Using the two-body Green's function (468) may be displayed in the form

$$\Omega_R^{\alpha 1} = - \tau^{-1} \int_0^\tau \cdots \int F_{\alpha 1, \beta 1}^{(R)} \cdot \nabla_{p_{\alpha 1}} K^{(2)}(\alpha 1, \beta 1, t)\, d\underline{R}_{\beta 1}\, d\underline{p}_{\beta 1}\, d\underline{R}'_{\alpha 1}\, d\underline{p}'_{\alpha 1}\, d\underline{R}'_{\beta 1}\, d\underline{p}'_{\beta 1}\, ds. \tag{476}$$

In the Rice-Allnatt theory the repulsive potential is taken to be an infinitely repulsive hard core. Thus $\underline{F}^{(R)}_{\alpha 1, K1} = 0$ except in the time interval $(0, 0+)$ and $\Omega^{\alpha 1}_{R} = 0$ in $0+ < t < \tau$. Note that $\underline{F}^{(R)}_{\alpha 1, j2} = 0, \ j \geq 2$ and $F^{(R)}_{\alpha 1, \beta K} = 0, \ K \geq 2$.

In Eq. (475) the integrals on the right-hand side of the equation vanish. Thus Eq. (475) may be solved for $-\underline{F}^{(R)}_{\alpha 1, \beta 1} \cdot \nabla_{P_{\alpha 1}} K^{(2)}(\alpha 1, \beta 1; s)$ and the result substituted in Eq. (476). After noting that $\underline{F}^{(R)}_{\beta 1, \alpha 1} \cdot \nabla_{P_{\beta 1}} K^{(2)}(\alpha 1, \beta 1; s)$ integrates to zero it is found that

$$\Omega^{\alpha 1}_{R} = \tau^{-1} \int_{0}^{\tau} \cdots \int \left[\frac{\partial K^{(2)}(\alpha 1, \beta 1)}{\partial s} + \frac{1}{m_{\alpha}} \underline{P}_{\alpha 1} \cdot \nabla_{R_{\alpha 1}} K^{(2)} + \frac{1}{m_{\beta}} \underline{P}_{\beta 1} \cdot \nabla_{P_{\beta 1}} K^{(2)} \right] f^{(2)}(\alpha 1, \beta 1; t)\, d\underline{R}_{\beta 1}\, d\underline{P}_{\beta 1}\, d\underline{R}'_{\alpha 1}\, d\underline{P}'_{\alpha 1} \times d\underline{R}'_{\beta 1}\, d\underline{P}'_{\beta 1}\, ds. \tag{477}$$

During the time interval $(0, 0+)$, $K^{(2)}(\alpha 1, \beta 1)$ satisfies a Liouville equation in pair space, a solution of which is

$$K^{(2)}(\underline{R}_{\alpha 1} \underline{P}_{\alpha 1} \underline{R}_{\beta 1} \underline{P}_{\beta 1} \mid \underline{R}'_{\alpha 1} \underline{P}'_{\alpha 1} \underline{R}'_{\beta 1} \underline{P}'_{\beta 1}; s) = \prod_{i=\alpha 1}^{\beta 1} \delta(\underline{R}_i - \underline{R}'_i - \Delta \underline{R}_i)\, \delta(\underline{P}_i - \underline{P}'_i - \Delta \underline{P}'_i). \tag{478}$$

With the substitution $f^{(2)}(\alpha 1, \beta 1) = g_0^{(2)}(\underline{R}_{\alpha 1}, \underline{R}_{\beta 1}) f^{(1)}(\underline{R}_{\alpha 1} \underline{P}_{\alpha 1}) f^{(1)}(\underline{R}_{\beta 1} \underline{P}_{\beta 1})$, integration over the indicated volume leads to

$$\Omega_R^{\alpha 1} = J_{1\alpha\beta} + J_{2\alpha\beta} , \tag{479}$$

where

$$\begin{aligned} J_{1\alpha\beta} = g_0^{(2)}(\sigma_{\alpha\beta}) \int\cdots\int \Big[& \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\alpha 1} - \Delta \underline{P}_{\alpha 1}; t) \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\beta 1} - \Delta \underline{P}_{\beta 1}) \\ & - \bar{f}^{(1)}(R_{\alpha 1}, P_{\alpha 1}; t) \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\beta 1}; t) \Big] \left| \frac{\underline{P}_{\alpha 1}}{m_\alpha} - \frac{\underline{P}_{\beta 1}}{m_\beta} \right| b\,db\,d\varepsilon\, d\underline{P}_{\alpha 1} \end{aligned} \tag{480}$$

$$\begin{aligned} J_{2\alpha\beta} = g_0^{(2)}(\sigma_{\alpha\beta}) \int\cdots\int \Big[& \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\alpha 1} - \Delta \underline{P}_{\alpha 1}; t) \sigma_{\alpha\beta} \underline{K} \cdot \nabla_{R_{\alpha 1}} \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\beta 1} - \Delta \underline{P}_{\beta 1}; t) \\ & - \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\alpha 1}; t) \sigma_{\alpha\beta} \underline{K} \cdot \nabla_{R_{\alpha 1}} \bar{f}^{(1)}(\underline{R}_{\alpha 1}, \underline{P}_{\beta 1}; t) \Big] \left| \frac{\underline{P}_{\alpha 1}}{m_\alpha} - \frac{\underline{P}_{\beta 1}}{m_\beta} \right| b\,db\,d\varepsilon\, d\underline{P}_{\beta 1} . \end{aligned} \tag{481}$$

From the relations

$$\Omega_s^{\alpha 1} = -\tau^{-1}\int_{0+}^{\tau}\int \underset{\sim}{F}^{(s)}_{\alpha 1,\beta 1}\cdot\nabla_{p_{\alpha 1}} f^{(2)}(\alpha 1,\beta 1;t+s)\,d\underline{R}_{\beta 1}\,d\underline{P}_{\beta 1}\,ds$$

$$-\tau^{-1}\int_{0+}^{\tau}\int \underline{F}^{(s)}_{\alpha 1,\alpha 2}\cdot\nabla_{p_{\alpha 1}} f^{(2)}(\alpha 1,\alpha 2;t+s)\,d\underline{R}_{\alpha 2}\,d\underline{P}_{\alpha 2}\,ds,$$

$$\Omega_s^{\alpha 1} = \Omega_s^{\alpha 1,\alpha 2} + \Omega_s^{\alpha 1,\beta 1} \tag{482}$$

using the same techniques as Rice and Allnatt and Ross, it is found that

$$\Omega_s^{\alpha 1} = (\zeta_{\alpha\alpha} + \zeta_{\alpha\beta})\,\dot{A}^{(1)}_{\alpha 1}\,\bar{f}^{(1)}(\alpha 1) - \nabla_{p_{\alpha 1}}\cdot\underline{F}^{*}_{\alpha 1}\,\dot{f}^{(1)}(\alpha 1). \tag{483}$$

With the final definitions

$$\underset{\sim}{A}^{(1)}_{\alpha 1} = \nabla_{p_{\alpha 1}}\cdot\left[\frac{1}{m_\alpha}\underset{\sim}{P}_{\alpha} + \kappa T\,\nabla_{p_{\alpha 1}}\right] \tag{484}$$

$$\mathcal{D}^{(1)}_{\alpha 1}\,\bar{f}^{(1)}(\alpha 1) = \left[\mathcal{L}_{\alpha 1} + \nabla_{p_{\alpha 1}}\cdot F^{*}_{\alpha 1}\right]\bar{f}^{(1)}(\alpha 1).$$

we obtain the desired form of the equation

$$\mathcal{D}_{\alpha 1}^{(1)} f^{(1)}(\alpha 1) = J_{1\alpha\beta} + J_{2\alpha\beta} + (\zeta_{\alpha\alpha} + \zeta_{\alpha\beta}) A_{\alpha 1}^{(1)} \bar{f}^{(1)}(\alpha 1) . \tag{485}$$

which has the solution given in section 2 of chapter III.